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THE PLACE FOR THERMOPLASTIC COMPOSITES IN
STRUCTURAL COMPONENTS

Report of the
Committee on Thermoplastic Composites as Structural Components

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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ABSTRACT

The potential for the development of thermoplastic matrix, carbon-fiber composites as structural materials is evaluated. Compared to thermoset matrices, thermoplastics appear to offer increases in toughness and durability while offering the potential for more cost-effective manufacturing methods. Both long- and short-fiber systems are described. The properties of thermoplastics are compared with those of thermoset matrix materials. The committee recommends that significant investments be made in the development of innovative, large-scale technologies for the cost-effective manufacture of long-fiber thermoplastic composite components and systems. Other recommendations are made for advanced characterization, including prediction methodology for the mechanics of time-dependent behavior.

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EXECUTIVE SUMMARY

This report examines the emerging field of thermoplastic composite materials and presents several conclusions regarding the potential of these materials for future applications. An assessment of the attributes and limitations of this class of materials was requested by the sponsors of the study to provide a basis for decisions on whether to invest greater resources in this technical area.

Thermoplastic composites possess a combination of properties that appear to be superior to currently used materials for some aerospace and land-based applications. Significant attributes include higher heat resistance and greater impact strength than are possessed by current composites incorporating conventional thermosetting polymers. For example, service temperatures of 350°F (compared to 200°F) and toughness about 2 to 3 times that of composites made from epoxies are possible. Better manufacturability may alone provide the major reason for using thermoplastics. However, since these composites are relatively new, unanswered questions remain about processability, solvent resistance, and optimum compositions. Thermoplastic composites have likewise demonstrated a potential for improved durability and favorable economics. Again, however, the limited data base and lack of industrial experience make uncertain any prediction as to their probable success.

In traditional materials development, experience was first gained with the production of small parts in secondary structures before any major commitment was contemplated. However, in the current era of rapid technological development, new materials systems and further innovations are brought rapidly from introduction to application. This rapid development has precluded generation of a broad base of experience in a variety of applications. At the same time, a detailed science base for thermoplastic composites has not been developed.

Short-fiber-reinforced thermoplastics have been available for more than 2 decades. Short-fiber reinforcement results in relatively modest enhancement of properties such as strength and stiffness when compared with the enhancement achieved by continuous-fiber reinforcement. One of the greatest virtues of these short-fiber-reinforced thermoplastics, however, is

their ease of processing--both as to speed and the ability to produce complicated, detailed parts. Thus they have already become established in automotive, electronic, and chemical processing applications, and they lend themselves to many uses in such categories as power tools, mixing valves, and water engineering components, particularly the more demanding applications in these categories.

The report discusses both short- and long-fiber-reinforced composites. Only long-fiber composites have strength properties superior to those of aluminum alloys, thus making them of interest as components of primary structures (where, indeed, the weight savings over aluminum alloys range from 25 to 50 percent). Nevertheless, short-fiber-reinforced thermoplastic composites are used in secondary structures where the tensile loading is less than 30,000 psi.

In broad general terms, the committee concluded that thermoplastic composites have potential for significantly improved durability over thermoset materials. In addition, significant reductions in manufacturing costs are possible if large-scale processing techniques for long-fiber thermoplastic composites could be developed. The promise already exhibited by thermoplastic composites is sufficient to lead to strong recommendations for specific studies that could accelerate confidence in their use.

The report generally recommends that the research and programs needed to move thermoplastic composite materials to an equivalent level of acceptance with contemporary thermoset systems be pursued. The committee's highest priority recommendation was that significant investment be made in the development of innovative large-scale processing techniques for cost-effective manufacturing of long-fiber thermoplastic composite components. Other important recommendations include development of characterization methods and limited data-base development for the currently available advanced thermoplastic composites to assess their relative merits. Innovative joining processes should also be investigated, including mechanical fastening and bonding. The most difficult recommendation to pursue is the development of new synthesis methods that use low-melting-point starting materials that polymerize to high-molecular-weight polymers without evolution of volatiles.

The use of composites in military and aerospace applications is determined principally by performance; cost is generally of secondary importance. The subsequent development of low-cost raw materials and cost-effective manufacturing techniques traditionally leads to the use of these composites in industrial applications. In view of their fabricability, strength, light weight, and corrosion resistance, such materials might offer advantages over existing materials in a variety of nonmilitary applications (for example, in components for cars, buses, and trains and in piping and structural elements in buildings).

The committee's detailed conclusions and recommendations are presented in Chapter 1. In other chapters, the characteristics and properties of thermoplastic polymers are described and compared with those of thermosets. Processing techniques, fabrication mechanisms, joining methods, and quality control technology are also discussed.

Chapter 1

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Thermoplastics Versus Thermosets

- Thermoplastic matrix composites have the potential for significant improvements in durability over thermosets.
- Most properties of thermoplastic composites are equivalent to those of thermosets. However, matrix-dominated properties such as compressive strength, time-dependent characteristics, and interlaminar behavior may be significantly different; for example, thermoplastic composites in general can exhibit more favorable strength and toughness than composites made with thermosetting resins, but time-dependent characteristics such as creep behavior (for which data are limited) may be inferior.
- Thermoplastic prepregs possess shelf life superior to thermoset systems.
- Thermoplastic matrix composites have the potential for significant reductions in cost of manufacturing over thermosetting composites.

Processing and Manufacturing

- Large-scale processing techniques for long-fiber thermoplastic composites have not yet been developed.
- Crystalline morphology strongly influences composite properties for semi-crystalline thermoplastic polymers.
- Certain polymers offer the potential for processibility both by conventional thermoplastic methods and, in monomeric form, by thermoset technology.

Interfaces

- The role of the fiber-matrix interaction in determining composite properties is not well understood.

- Conventional fiber surface finishes and treatments for adhesion to thermoset polymers may not be appropriate for thermoplastics.

Other

- Certain thermoplastic polymers offer significant resistance to the action of solvents and to environmental degradation.
- Appropriate data bases do not exist for thermoplastic composites.

PRIORITIZED RECOMMENDATIONS

	<u>Difficulty*</u> (10-1)	<u>Importance</u> (10-1)
Significant investments should be made in the development of innovative large-scale processing techniques for cost-effective manufacturing of long-fiber thermoplastic composite components.	5	10
Characterization methods and a limited data base should be developed for the available, advanced thermoplastic composite material systems to assess their relative merits.	8	9
New synthesis methods that use low melting starting materials and polymerize to high molecular weight polymer without evolution of volatiles need to be developed.	9	9
Synthesis of new processible thermoplastic polymers that possess enhanced elevated-temperature performance should be explored.	8	8
The influence of fiber surface finish and treatment on the properties of thermoplastic composites should be investigated.	6	8
The investigation of crystalline polymer morphology as it relates to composite properties should be accelerated.	6	7
The relationship between rheological behavior of thermoplastic polymers and the processing characteristics of their composites needs investigation.	6	7

*10 being most difficult or important

	<u>Difficulty</u> (10-1)	<u>Importance</u> (10-1)
Simulations for the processing of thermoplastic composites should be developed to model heat transfer, polymeric flow, phase change, and fiber orientation phenomena.	7	8
The time-dependent characteristics of thermoplastic composites including stress relaxation, fatigue, creep rupture, and rate sensitivity should be investigated.	6	8
Methods to evaluate <i>in situ</i> crystalline morphology of thermoplastic composites require development.	8	7
The factors that control fiber orientation distribution during processing of short-fiber thermoplastic composites should be investigated, and both characterization and simulation methods should be developed.	8	8
The characterization and prediction of time-dependent behavior (creep, stress relaxation, dynamic mechanical properties) are key to the advancement of short-fiber thermoplastic composite technology and should be key research areas in any development plan for these materials.	7	8
Innovative joining processes including mechanical fastening, bonding, and especially welding should be investigated.	7	10

Chapter 2

INTRODUCTION

Thermoplastic composites have only recently been considered for use as structural components. A number of interrelated issues have stimulated the debate.

The past 15 years have seen an increasing reliance on resin-matrix composites for structural components in aircraft, spacecraft, and a limited number of ground transportation systems. Epoxy resin, a thermosetting plastic, has been the preferred matrix, principally because of its reasonable balance among performance, cost, processibility, and environmental stability.

It may well be expected that future advancements in thermoset technology will yield materials with elevated temperature and toughness properties equivalent to thermoplastics as they now exist. Thermoformability and weldability of thermoplastics may alone differentiate them from thermosets in the future. Historically, two deficiencies of epoxy resins have created pressure to find new matrix materials. First, the processing costs of epoxy have resulted in limiting the range of components to which they can be applied. Second, the low resistance to damage from through-the-thickness impact of laminates has eroded confidence in the post-impact performance, raising questions about compression behavior, fuel leakage in composite tanks, and repair issues in general.

By replacing the thermosetting resin matrix with a thermoplastic one, potential deficiencies in epoxy technology of the early 1980s could simultaneously be mitigated. Until recently, the solvent sensitivity of candidate thermoplastic systems has prevented them from being seriously considered. Now, however, a number of solvent-resistant candidates have become available. Consequently, serious consideration is now being given to fiber-reinforced thermoplastic composites. Such consideration is focused on the behavioral differences between thermosets and thermoplastics, and especially on the cost, processing, and durability issues. The introduction of new high-temperature thermoplastics has made the competition even more interesting.

The report considers only isotropic thermoplastic polymeric materials, and thereby has excluded consideration of liquid crystalline polymers and molecular composites. The remainder of this report addresses these issues with the objective of pointing out the key factors dictating the intelligent use of thermoplastic composites as structural components.

Chapter 3

PROPERTIES

The period between approximately 1930 and 1960 may well go down in history as the "Plastics Age." During this period, significant progress was made in the synthesis and commercialization of many plastic materials that have become an integral part of our lives. Since 1960 there has been increasing emphasis placed on development of higher strength, higher performance plastic materials. During this period, several new high-performance resins have been commercialized as a class of materials known as engineering plastics (e.g., polyamides, polyarylene ethers and sulfides, polyetherimides, polyamideimides, polysulfones, and polyesters). These engineering plastics are generally characterized by attractive properties that include thermal stability, high strength, high modulus, solvent resistance, retention of properties at elevated temperatures, etc. Certain of these properties may be enhanced by addition of fiber reinforcement. Properties most often improved include strength, modulus, creep resistance, fatigue, dimensional stability, heat distortion temperature, and, in certain cases, impact strength. Historically, most emphasis has been placed on short-fiber reinforcement. Thus, many of the engineering plastics are now available as injection molding compounds containing short fiber (e.g., less than 750 μm in the molded part) reinforcement.

Recently, considerable effort has been devoted to development of a new class of materials, advanced thermoplastic composites, based on long-fiber reinforcement of thermoplastic resin matrixes. Properties of these composite materials are maximized by careful alignment of continuous reinforcing fibers in the load direction.

Although properties of these three classes of materials (i.e., base resin, short-fiber reinforced, and long-fiber reinforced) vary slightly within each class, they represent three distinctly different performance categories. General property ranges are shown in Figure 3-1. Detailed properties are discussed in appropriate sections of this report.

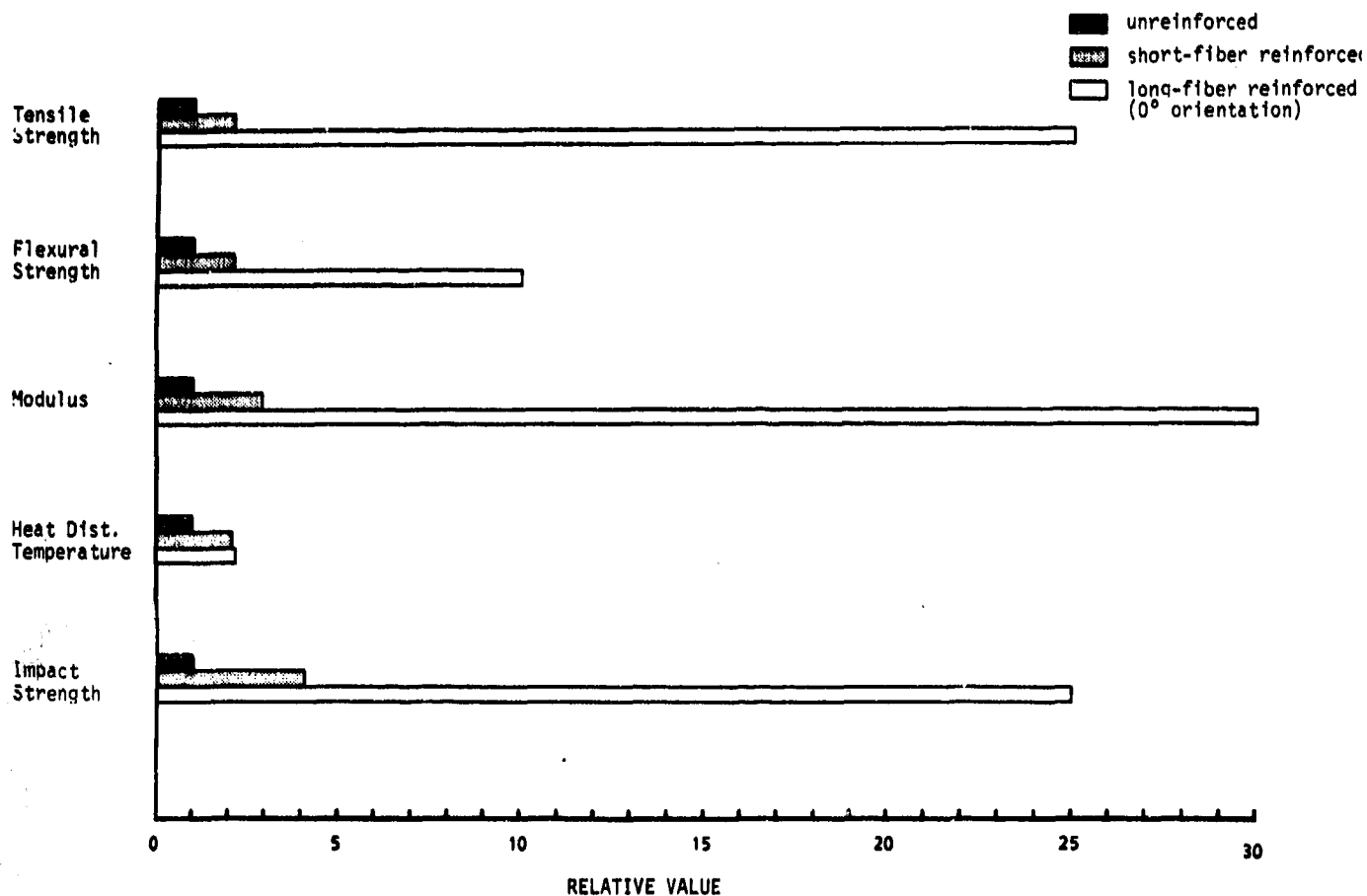


FIGURE 3-1 Nominal relative properties of thermoplastic materials. (Typical values for unreinforced engineering thermoplastic resins: tensile strength, 10 to 15 ksi; flex strength, 15 to 25 ksi; flex modulus, 400 to 600 ksi; heat distortion temperature, 280 to 500°F; and notched impact, 0.5 to 2.5 ft·lb·in.)

NEAT RESINS AND PROPERTIES

This section presents the molecular structures of thermoplastics used as matrixes in carbon-fiber-reinforced composites and discusses neat resin properties such as thermal performance, processibility, fracture toughness, and solvent resistance.

Molecular Structure and Thermal Properties

Table 3-1 lists 21 commercially available high-performance thermoplastics derived from seven classes of organic functional groups. An idealized chemical formula is shown for each polymer if known from published literature or estimated from trade sources. While this list is not exhaustive, it is representative of thermoplastics, both amorphous and semicrystalline, that have been or are being investigated as matrix materials for high-performance composites. Table 3-2 gives the approximate values for glass transition

TABLE 3-1 High-Performance Thermoplastics



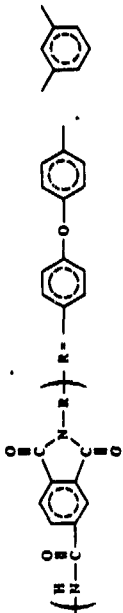

Number	Generic Name	Company	Trade Name	Formula
<u>Polyethers and Thioethers</u>				
I	polyetheretherketone (PEEK)	Imperial Chemical Industries	Victrex PEEK	
II	polyaryleneketone (HTX)	Imperial Chemical Industries	Victrex HTX	N/A
III	polyaryleneketone	Amoco Performance Products	PXM-8505	N/A
IV	polyphenylene sulfide (PPS)	Phillips Petroleum Company	Ryton	
V	polyarylenesulfide (PAS-2)	Phillips Petroleum Company	Ryton PAS-2	N/A
<u>Polyamides</u>				
VI	polyamideimide (PAI)	Amoco Chemicals Corporation	Torlon	
VII	polyamideimide	Amoco Performance Products	Torlon AIX 638/696	N/A
VIII	PACM polyamide	E. I. Du Pont de Nemours and Co., Inc.	J-2	

TABLE 3-1 High-Performance Thermoplastics (continued)

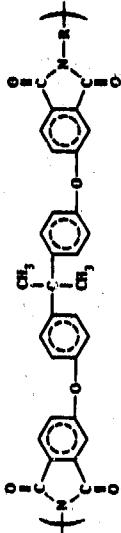
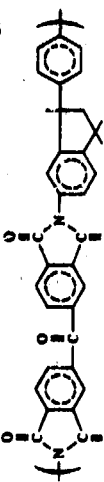
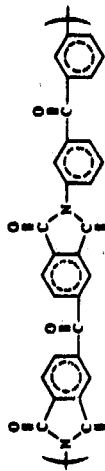
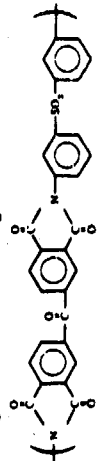
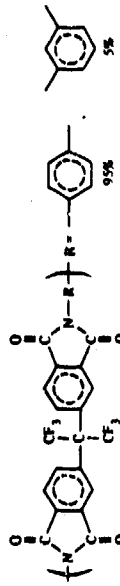

Number	Generic Name	Company	Trade Name	Formula
Polyimides				
Polyimides				
IX	polyetherimide (PEI)	General Electric Company	Ultem 1000	
X	polyindaneimide	Ciba-Geigy Corporation	XU-218	
XI	polyketonimide	Mitsui Toatsu Chemicals, Inc.; Rogers Corp.	LARC-TPI	
XII	polyimidesulfone	High Tech Services	PISO ₂	
XIII	polyaryleneimides	E. I. duPont de Nemours and Company, Inc.	Avimid K-III	N/A
XIV	polyaryleneimide	E. I. duPont de Nemours and Company, Inc.	Avamid N (NR150B2)	
XV	polyaryleneimide	The Upjohn Company	2080	

TABLE 3-1 High-Performance Thermoplastics (continued)

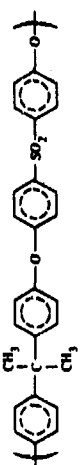


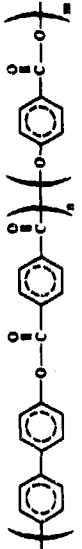
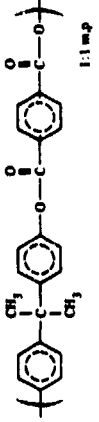
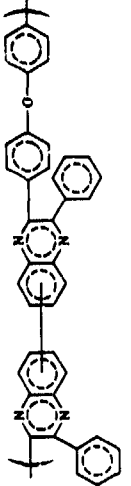
Number	Generic Name	Company	Trade Name	Formula
Polysulfones				
polyarylene ether sulfones				
XVI		Amoco Performance Products	UDESL P1700	
XVII		Amoco Performance Products	Radel A400	
XVIII		Imperial Chemical Industries	Victrex PES 4100G	
Polyesters				
XIX	liquid crystalline	Dartco Mfg., Inc.	Xydar SRT-300	
XX	arylene	Amoco Performance Products	Ardel D-100	
Polyphenylquinoxaline				
XXI	ether phenyl-quinoxaline	Philip A. Hunt Chemical Corp.	PPQ	

TABLE 3-2 Thermal Properties of Some High-Performance Neat Thermoplastics

Number	Trade Name	T _g (°C)	T _m (°C)	HDT (°C) ^a	UL (°C) ^b	Processing Temp. Range (°C)
I	Victrex PEEK	143	343	152	--	370 to 400
II	Victrex HTX	205	386	--	--	400 to 420
III	PXM-8505	265	None	--	--	--
IV	Ryton PPS	90	290	115	200 to 240	315 to 340
V	Ryton PAS-2	215	None	198	--	325 to 330
VI	Torlon	275	None	274	200	330 to 400
VII	Torlon AIX 638/696	243	None	--	--	325 to 350
VIII	J-2	156	None	154	--	295 to 315
IX	Ultem 1000	217	None	200	170	340 to 400
X	XU-218	320	None	--	--	350 to 427
XI	LARC-TPI	264	None	--	--	340 to 427
XII	PISO ₂	273	None	--	--	350
XIII	Avimid K-III	251	None	--	--	340 to 400
XIV	Avimid N	360	None	--	--	350 to 400
XV	2080	310	None	270 to 280	--	325 to 350
XVI	Udel P1700	190	None	174	150	315 to 370
XVII	Radel A400	220	None	204	--	330 to 370
XVIII	Victrex PES 4100G	230	None	203	180	315 to 370
XIX	Xydar SRT-300	--	421	355	240	360 to 430
XX	Ardel D-100	188	None	174	130	315 to 370
XXI	PPQ	290	None	--	--	350 to 400
--	3501-6 Epoxy ^c	206	None	--	--	177
--	8551-7 Epoxy ^d	182	None	--	--	177

^aHeat distortion temperature at 264 psi, ASTM D648^bUnderwriter's Laboratory temperature index rating^c177°C cure epoxy based on tetraglycidylether of bisphenol A backbone cured with 4,4'-diaminodiphenylsulfone, a product of Hercules, Inc.^dMultiphase toughened epoxy, a product of Hercules, Inc.

temperature (T_g), melt temperature (T_m) [semicrystalline polymers], heat distortion temperature, U.L. temperature index rating, and processing temperature range for each polymer.

All of these polymers are made by condensation polymerization techniques and generally have molecular weights above 20,000. Only two materials, Avimid K-III and Avimid N (XIII and XIV in Table 3-1), are made available as a mixture of monomers in solution, which requires the polymerization process to be effected *in situ* during fabrication with the evolution of volatiles. The remaining polymers are available and must be processed as "high" molecular-weight materials. It is assumed that polymer molecular weight is or can be controlled to achieve an optimum compromise between processibility and other properties.

Another similar characteristic of these high-performance thermoplastics is the dominant aromatic character in their molecular structure. The presence of phenyl groups in the main chain helps keep T_g values sufficiently high so that these polymers can be effectively utilized as structural materials at 100 to 125°C or higher for long periods. A high degree of aromaticity also tends to afford the higher tensile and shear properties required for structural applications. However, in all cases, the aromatic rings are separated by groups such as ether, carbonyl, thioether, amide, methylene, isopropylidene, ester, and sulfone, which help make the polymer chains flexible for ease of processing.

Processing

In general, because thermoplastics are high-molecular-weight materials and have high melt viscosities even at elevated temperatures, they must be fabricated far above their heat distortion temperatures and usually well above 300°C, in contrast to most of the oligomeric epoxy-type thermosets that are fabricated at 177°C. Table 3-2 lists thermal properties of the 21 polymers shown in Table 3-1. High processing temperatures are required to achieve the low melt viscosity required in composite fabrication for good consolidation and good filament wetting. A melt viscosity of 10^2 to 10^4 poise at standard shear rates is desirable for fabrication of composites and adhesive bonds. For example, composites from Udel P1700 polysulfone (Table 3-1, number XVI) are fabricated at 343°C; its melt viscosity at 343°C is 10^4 poise; at 385°C, the melt viscosity is half that value. The semicrystalline polymers (Table 3-1, numbers I and IV) have much lower T_g values than the amorphous materials but must be processed in excess of the melt temperature of the semicrystalline phase to achieve low melt viscosities, good consolidation, and proper morphology. Composites from PEEK, I, for example, have to be processed at 385°C to 400°C, temperatures where its melt viscosity is between 4000 and 5000 poise. Maximum use temperatures of these materials can be controlled either by T_g or T_m , depending on the degree of crystallization.

All of the thermoplastics in Table 3-2 have use temperatures at or above 130°C, certainly above the temperature requirements for most structural applications in subsonic transports. Many have use temperatures in the 170°C to 180°C range required for applications on supersonic fighter and supersonic

commercial aircraft. Indeed, these materials seem to offer a wide operational temperature capability that covers all but the most stringent of needs, provided other property requirements are met.

Table 3-3 lists neat resin tensile and flexural properties of the 21 high-performance thermoplastics. Several have sufficient modulus values (greater than 450 to 600 ksi) to afford acceptable resin-dominated composite stiffness properties such as 0° compressive strengths (greater than 200 ksi) at room temperature. Acceptable modulus values under hot and hot/wet conditions are key design requirements in aircraft; unfortunately, this information is not available for most of the neat materials in Table 3-3. Neat resin shear or tensile moduli can be used to effectively predict composite 0° compressive strength by using the relationship recently established by Hahn and Williams (1984) (Figure 3-2).

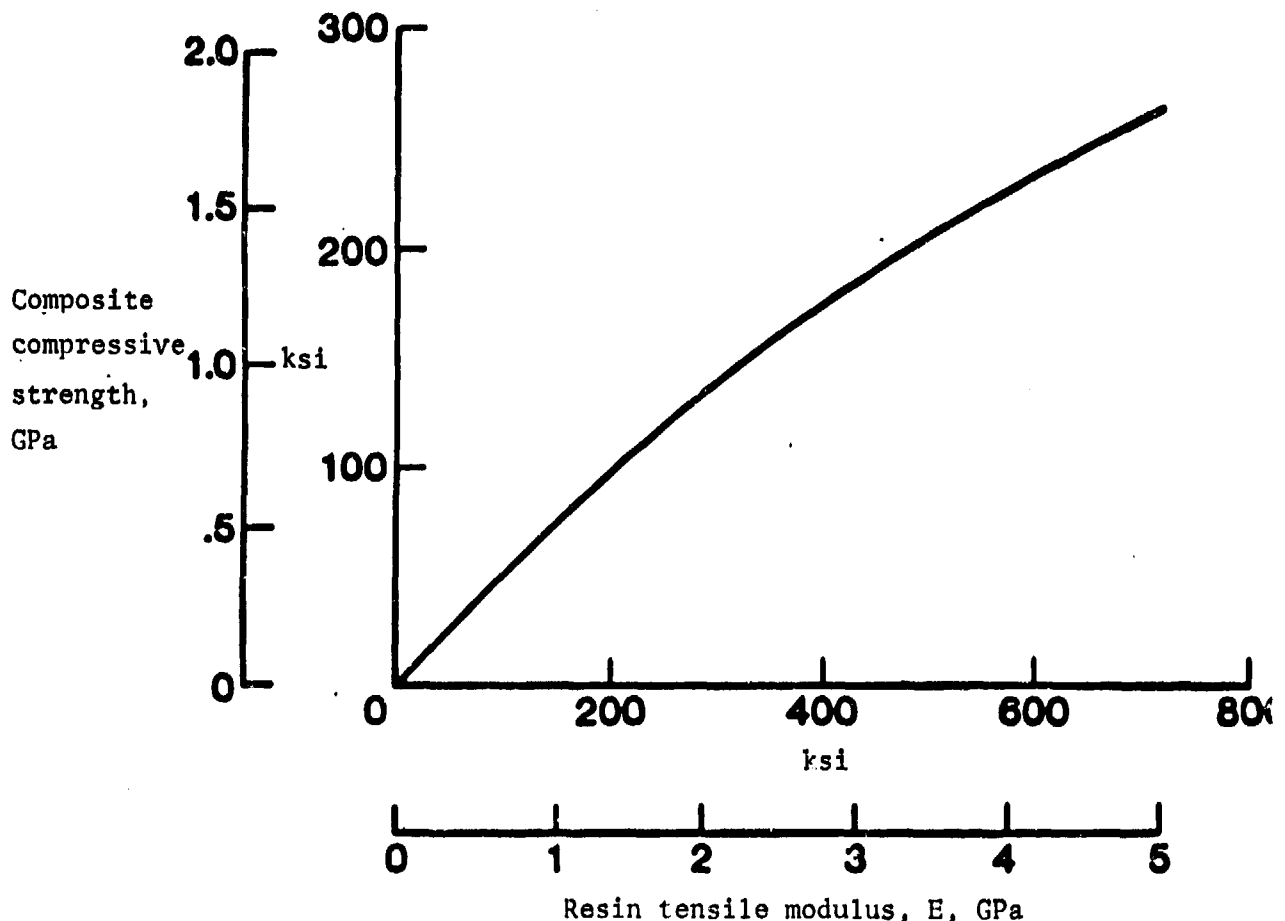


FIGURE 3-2 Composite compressive strength versus resin tensile modulus (Hahn and Williams, 1984).

TABLE 3-3 Mechanical Properties of Selected High-Performance Neat Resin Thermoplastics^a

Number	Name	Tensile Properties			Strain to Break, %			Flexure Properties			Modulus, ksi		
		Strength at Yield, ksi			Modulus, ksi			Strength, ksi			RT		
		RT	100°C	149°C	RT	100°C	149°C	RT	100°C	149°C	RT	100°C	149°C
I	Victrex PEEK	14.5	9.6	5.1	0.450	40	16	--	--	--	0.565	0.435	0.290
II	Victrex HTX	--	--	--	0.450	--	--	--	--	--	--	--	--
III	PM-8505	12.7	--	--	0.360	13	--	--	--	--	--	--	--
IV	Ryton PPS	12.0	--	--	0.630	3 to 5	24	--	--	--	0.590	--	--
V	Ryton PAS-2	14.5	--	--	0.400	7.3	25.7	--	--	--	0.470	--	--
VI	Torlon	24.1	22.0	18.0	0.530	12 to 15	30	28	24	--	0.630	--	--
VII	Torlon AIX	13.0	--	--	0.400	30	--	--	--	--	--	--	--
	638/696												
VIII	J-2	12.3	--	--	0.461	44.3	18.2	--	--	--	0.430	--	--
IX	Ultem 1000	15.2	13.0	11.0	0.430	60	21	--	--	--	0.480	0.450	0.390
X	XU-218	12.6	--	--	0.420	49	--	--	--	--	--	--	--
XI	LARC-TPI	17.3	--	--	0.540	4.8	--	--	--	--	--	--	--
XII	PISO ₂	9.1	--	--	0.719	1.3	--	--	--	--	--	--	--
XIII	Avimid K-III	14.8	--	--	0.546	14	--	--	--	--	--	--	--
XIV	Avamid N	16.0	13.0	11.0	--	6	17.0	--	--	--	0.605	--	--
XV	2080	17.1	--	--	0.188	10	28.8	22	19	--	0.481	0.400	0.350
XVI	Udel P1700	10.2	7.5	6.0	0.360	50 to 100	15.4	--	--	--	0.390	0.360	0.310
XVII	Radel A400	10.4	--	--	0.380	60	12.4	--	--	--	0.330	--	--
XVIII	Victrex PES	12.2	10.0	8.0	--	40 to 80	18.7	--	--	--	0.380	0.370	0.360
	4100C												
XIX	Xydar SRT-300	19.0	9.0	5.0	2.100	1.3	19.0	--	--	--	2.000	1.600	1.400
XX	Ardel D-100	9.5	--	--	0.290	50	11.0	--	--	--	0.310	--	--
XXI	PPQ	17.0	--	--	0.380	8.5	--	--	--	--	--	--	--
-	3501-6 Epoxy	12.0	--	--	0.620	1.2	--	--	--	--	--	--	--
-	8551-7	--	--	--	--	--	--	--	--	--	--	--	--

^aTo convert ksi to MPa or ksi to GPa, multiply by 6.9.

Fracture Toughness Properties

Neat resin G_{Ic} fracture toughness values from compact tension tests are shown in Table 3-4. The values are generally above 14 in.-lb/in.² (2500 J/m²) and are to be contrasted with the much lower values, 0.4 to 0.5 in.-lb/in.² (69 to 95 J/m²), observed for the brittle 177°C cure epoxies used as matrixes in current high-performance composites. They are also higher than the fracture toughness values for the second generation of toughened epoxies now available, 1.1 to 2.9 in.-lb/in.² (200 to 600 J/m²), and much larger than those observed for high-temperature thermosetting polyimides such as PMR-15, LARC-160, and various first-generation bismaleimides. These outstanding values are one of the reasons thermoplastics are desirable as matrixes in high-performance composites.

Notched Izod impact energies also are listed in Table 3-4. This popular fracture toughness measurement would not be expected to correlate with the G_{Ic} test, although values above 1 ft-lb/in. are indicative of tough materials.

Very little has been done to relate tensile and compression creep of neat resins to similar data in composites. The limited data given in Table 3-4 indicate that some of these thermoplastics can undergo creep; the severity of the creep problem and its effect on composites remain to be determined.

Solvent Resistance

Table 3-5 shows the effect of solvents on most of the thermoplastics of interest. Poor resistance to various organic fluids can be a serious detriment to the utilization of thermoplastics in structural applications. Composites under load must be resistant to swelling and delamination in the presence of fuel, fuel additives, antifreeze, paint strippers, and hydraulic fluid. Many of the thermoplastics in Table 3-5 do not exhibit the fluid resistance necessary for exploitation in aircraft structural applications. In some of these cases, attempts are being made to increase resistance to fluids by inducing limited cross-linking into the polymer backbone through the use of annealing, postcures, or thermal reactions of terminal and pendant norbornene, ethynyl, and phenylethynyl groups. Limited success has been achieved at a sacrifice in fracture toughness. In other materials, solvent resistance is achieved by crystallinity (numbers I, II, IV, and XIX in Table 3-1) or by unique chemical structure.

COMPOSITE PROPERTIES AND PERFORMANCE

This section presents the limited data available on mechanical and toughness properties of thermoplastic composites and a discussion of the susceptibility of composites to chemical warfare agents.

Continuous-fiber-reinforced thermoplastic composite structures must meet the same regulatory static, dynamic, and fail-safe loads as conventional thermosetting composites. The criteria and procedures used in aircraft

TABLE 3-4 Impact, Fracture Toughness, and Creep Properties of Selected High-Performance Neat Thermoplastics

Number	Name	Notched Izod ft-lb/in.	G_{Ic} in.-lb/in. ²	Tensile Creep
I	Victrex PEEK	1.6	>23	1.73% after 168 hr, 150°C, 1,450 psi
II	Victrex HTX	--	--	--
III	PMX-8505	--	--	--
IV	Ryton PPS	3.0	0.6 to 1.4	0.6 % after 1000 hr, 66°C, 5,000 psi
V	Ryton PAS-2	0.8	--	--
VI	Torlon	2.7	19.4	4.8 % after 1000 hr, 100°C, 15,000 psi 1.0 % after 100 hr, 23°C, 5,000 psi 1.7 % after 100 hr, 240°C, 5,000 psi
VII	Torlon AIX 638/696	--	20	
VIII	J-2	1.5	11.5	
IX	Ultem 1000	1.0	14.3	--
X	XU-218	--	--	--
XI	LARC-TPI	--	10	--
XII	PISO ²	--	8	
XIII	Avimid K-III	--	11	
XIV	Avimid N	0.8	13.7	--
XV	2080	0.7	--	--
XVI	Udel P1700	1.2	14	1.0% after 20,000 hr, 22°C, 3,000 psi 1.8% after 300 hr, 100°C, 3,000 psi 2.0% after 10,000 hr, 149°C, 1,000 psi
XVII	Radel A400	12.0	20	< 0.7% after 500 hr, 175°C, 1,000 psi
XVIII	Victrex PES 4100G	1.6	11	~ 1.0% after 24 hr, 150°C, 2200 psi
XIX	Xydar SRT-300	2.4	16.6	--
XX	Ardel D-100	4.2	--	2.5% after 3000 hr, 100°C, 3000 psi
XXI	PPQ	--	--	--
-	3501-6 Epoxy	--	0.7	--
-	8551-7 Epoxy	--	--	--

Note: To convert in.-lb/in² to J/m², multiply by 175

TABLE 3-5 Solvent Effects on Selected High-Performance Neat Thermoplastics^a

Number	Name	SKYDROL Hydraulic Fluid	JP-4	Alcohols Glycols	Chlorinated Hydrocarbons	Ethers	Ketones	Esters	Aromatic Hydrocarbons	WFR/ 20% DMAC	H ₂ O Uptake Saturation, %
I	Victrex PEEK	o	o	o	o	o	o	o	o	o	0.50
II	Victrex HTX	o	o	o	o	o	o	o	o	o	0.7
III	PM-8505	o	o	o	o	o	o	o	o	o	1.8
IV	Ryton FPS	o	o	o	o	o	o	o	o	o	0.4
V	Ryton PAS-2	o	o	o	o	o	o	o	o	o	o
VI	Torlon	o	o	o	o	o	o	o	o	o	2.0 to 5.0
VII	Torlon AIX	o	o	o	o	o	o	o	o	o	1.8
VIII	638/696	o	o	o	o	o	o	o	o	o	o
IX	J-2	+	o	+	+	+	+	+	+	+	5.0
X	Ultem 1000	o	o	o	o	o	o	o	o	o	1.2
XI	XU-218 ^b	+	o	o	o	o	o	o	o	o	0.9
XII	LARC-TPI	o	o	o	o	o	o	o	o	o	o
XIII	PISO ₂	o	o	o	o	o	o	o	o	o	o
XIV	Avimid K-III	o	o	o	o	o	o	o	o	o	2.2
XV	Avimid N	o	o	o	o	o	o	o	o	o	o
XVI	2080	o	o	o	o	o	o	o	o	o	o
XVII	Udel P1700	+	o	o	o	o	o	o	o	o	0.86
XVIII	Radel A400	+	o	o	o	o	o	o	o	o	1.3
XIX	Victrex PES	+	o	o	o	o	o	o	o	o	o
XX	4100G	o	o	o	o	o	o	o	o	o	o
XXI	Xydar SRT-300	o	o	o	o	o	o	o	o	o	0.2
XXII	Ardel D-100	+	o	o	o	o	o	o	o	o	0.71
XXIII	PFQ	o	o	o	o	o	o	o	o	o	o
XXIV	3501-6 Epoxy	o	o	o	o	o	o	o	o	o	o
XXV	8551-7 Epoxy	o	o	o	o	o	o	o	o	o	o

^a + = attacks or is absorbed; ++ = dissolves; o = no effect.^b Insoluble in all solvents after a 350°C, 1-hr postcure.

design over the past 2 decades have produced composite structures with an excellent performance record. The early composite designs generally employed a gross area strain limit to account for unknown deficiencies such as manufacturing anomalies, secondary load paths, and small area damage. Experience has shown that this composite design philosophy has been effective in allowing sufficient opportunities for weight reduction while not allowing detrimental out-of-plane loads or unacceptable stress concentrations. The capabilities of structures designed in this manner have been demonstrated by full-scale static and fatigue tests. Federal regulations and certification guidance material have been updated to reflect this philosophy and state-of-the-art developments in design, analysis, and testing. These criteria also require damage detection considerations in the inspection program and the limit load strength capability at all times. The application of thermoplastic composite materials as aircraft structural materials can be expected to build on the data base established for thermosetting composites. Modifications to the evaluation criteria can be expected as experience develops with this family of materials.

Mechanical Properties

Three principal considerations must be evaluated to achieve a balanced property design for application of thermoplastic composites as aircraft structural materials: static strength and stability, fatigue life or durability, and damage tolerance. Unfortunately, very little data, other than static strengths, primarily at room temperature, are available for thermoplastic composites because they are emerging new materials. Table 3-6 lists some room-temperature tensile, flexural, compressive, and shear properties for carbon fiber composites made from nine high-performance thermoplastics. Most of these properties compare favorably with the standard 177°C cure epoxies. Information on mechanical properties under hot and wet conditions is sorely needed for thermoplastic composites in order to better gauge their potential as aircraft structural materials.

Toughness

Table 3-7 lists impact and interlaminar fracture toughness properties of selected thermoplastic carbon fiber composites. In all cases, the interlaminar G_{Ic} values equal or far surpass a generally accepted goal of 4 to 6 in.-lb/in.² (700 to 1000 J/m²) for second-generation thermosets in structural applications involving civilian and military subsonic transports (see Figure 3-3). From the relationship shown in Figure 3-4, it can be seen that a goal of 4 to 6 in.-lb/in.² (700 to 1000 J/m²) for composite interlaminar fracture energy could be achieved with a resin fracture energy of 4.6 to 10.3 in.-lb/in.² (800 to 1800 J/m²), a range of values considerably lower than observed for many high-performance thermoplastics (see Table 3-4). It appears that interlaminar G_{Ic} values could be compromised considerably to obtain modified thermoplastic formulations having a better balance of properties such as processability and solvent resistance. It should be noted in Figure 3-4 that the highest fracture toughness values were obtained from 250°F cure rubber-toughened model thermosets whose hot/wet properties are very poor.

INTERLAMINAR FRACTURE TOUGHNESS OF COMMERCIAL GRAPHITE COMPOSITES

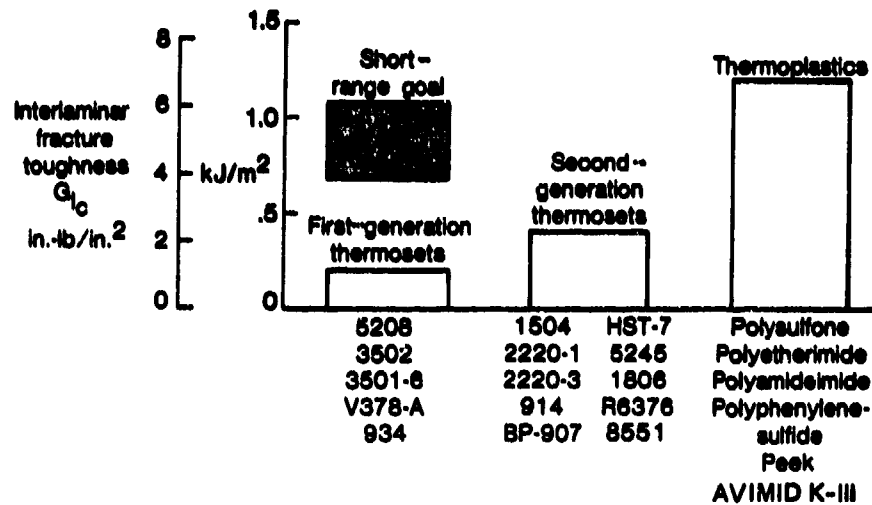


FIGURE 3-3 Interlaminar fracture toughness of commercial graphite composites.

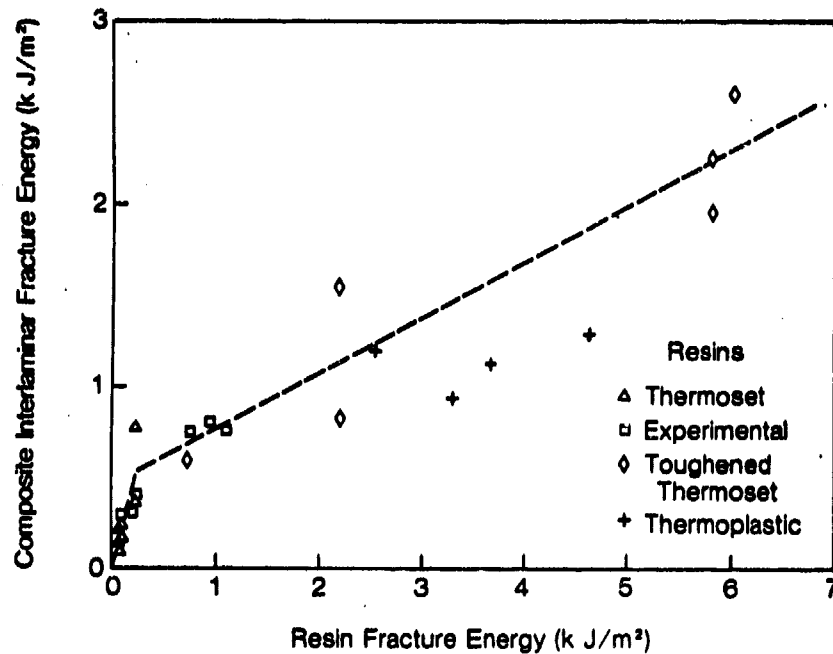


FIGURE 3-4 Influence of resin toughness on composite toughness (Hunston, 1984).

TABLE 3-6 Mechanical Properties of Carbon Fiber Composites Containing High-Performance Thermoplastic Matrixes^a

Number	Name	Fiber	0° Longitudinal			0° Transverse			Shear Modulus, ksi	0° Flex. Strength, ksi	0° Flex. Mod., ksi	0° SBS Strength, ksi	0° Compr. Strength, ksi
			Strength, ksi	Modulus, ksi	Strain, %	Strength, ksi	Modulus, ksi	Strain, %					
I	PEEK APC-2	AS4	309-356	19.4-20.5	1.45-1.6	11.6-11.9	1.29-1.5	1.0	0.74-0.91	273	19.4	15.2	150-160
II	APC-HXT	AS4	288	19.7	--	--	--	--	--	257	19.0	12.0	164
III	PAM-R505	--	--	--	--	--	--	--	--	--	--	--	--
IV	Ryton PPS	AS4	238	19.6	--	4.6	1.30	--	--	187	17.6	--	95
V	Ryton PAS-2	AS4	194	21.0	--	5.5	--	--	--	241	16.0	--	130
VI	Torlon C	C3000	200	20.6	--	--	--	--	--	300	18.5	16	200
VII	Torlon AIX	--	--	--	--	--	--	--	--	--	--	--	--
	638/696	--	--	--	--	--	--	--	--	--	--	--	--
VIII	J-2	AS4	--	--	--	5.0	1.3	--	--	210	17	15	152
IX	Ultem 1000	T300	--	19.7	--	--	1.21	--	0.71	--	--	--	--
XI	LARC-TPI	AS4	--	--	--	--	--	--	0.80	285	14.1	13.8	--
XII	PISO ₂	AS4	--	--	--	--	--	--	--	300	18.8	18.4	--
	LARC-TPI (2:1)	--	--	--	--	--	--	--	--	--	--	--	--
XIII	Aramid K-III	IM6	339	23.3	1.46	6.8	1.2	--	--	230	18.0	13.9	144
XIV	Aramid N	Celion	--	--	--	--	--	--	--	230	15	15.0	--
XV	Udel PI700	AS	193	18.7	--	8.6	1.00	--	--	251	18	16.0	--
		T300	155	20.5	--	--	0.81	--	--	214	14	14.3	151
XVIII	PES 4100G	HTS	--	--	--	--	--	--	0.48	--	--	11.5	--
XXI	PPQ	HTS	--	--	--	--	--	--	--	215	17.9	13.2	--
	3501-6 Epoxy	AS4	280	21.0	1.4	7.8	1.4	0.6	0.8	260	18.5	17.5	220
	8551-7	AS4	315	18.5	--	12.2	1.3	--	--	266	--	16.1	230

^aRoom temperature values

Note: To convert ksi to MPa or ksi to GPa, multiply by 6.9.

TABLE 3-7 Impact and Fracture Toughness Properties of Carbon Fiber Composites Containing High-Performance Thermoplastic Matrixes

Number	Name	Fiber	Compression After Impact ^a						G_{Ic} in.-lb/in. ^{2b}
			1000		1500		2000		
			in.-lb/in.		in.-lb/in.		in.-lb/in.		
			ϵ %	σ Ksi	ϵ %	σ Ksi	$\epsilon\sigma$ %	Ksi	
I	PEEK APC-2	AS4	--	48	--	45	--	42	10.7
II	APC-HTX	AS4	--	--	0.63	40	--	--	12.7
III	PXM-8505	--	--	--	--	--	--	--	--
IV	Ryton PPS	AS4 ^c	0.63	32	0.52	26	--	--	5.1
V	Ryton PAS-2	--	--	--	--	--	--	--	--
VI	Torlon C	C3000 ^d	0.96	53	0.93	50	0.83	46	10.0
VII	Torlon AIX 638/696	--	--	--	--	--	--	--	--
VIII	J-2	AS4	--	--	0.75	50	--	--	7.5
IX	Ultem 1000	AS4	--	--	--	--	--	--	6.1
XI	LARC-TPI	AS4	--	--	--	--	--	--	4.8
XII	PISO ₂ LARC-TPI (2:1)	AS4	--	--	--	40	--	--	7.0
XIII	Avimid K-III	IM6	0.60	43	0.57	40	0.51	37	8.1
XVI	Udel P1700	AS	--	--	--	--	--	--	6.9-7.7
	3501-6	AS4	0.32	26	0.34	21	0.31	19	1.0
	8551-7	IM7	--	--	0.79	53	--	--	3.1

^aQuasi-isotropic panels; data normalized to 1-in. thick specimens.

^bTo convert in. lb/in.² to J/m², multiply by 175.

^cAdditional values:

500 in.-lb/in. ϵ = 0.73, σ = 35 ksi

2500 in.-lb/in. ϵ = 0.41, σ = 19 ksi

3325 in.-lb/in. ϵ = 0.40, σ = 18 ksi

^d24 ply CSW (± 45)/(0,90)_{3s}

Post-impact compression strains of thermoplastic composites after 1000 and 1500 in.-lb/in. impact energies appear to be well above the required 0.60 percent strain necessary to achieve optimum weight saving compared to aluminum. This information is also needed for hot and hot/wet test conditions, since compression properties are resin-dominated.

Data on fatigue and creep properties of thermoplastic composites are very limited, and more research in this area is highly desired. Thermoset composites have been shown to be reasonably fatigue-resistant in tension and to have outstanding creep resistance. They offer challenging goals for thermoplastic composites to meet.

Environmental Considerations

The effects of the environment, including environmental cycling, and nondetectable damage apply to each of the three principal considerations cited earlier and must be accounted for in the design. The environmental design criteria should reflect the most critical environmental exposure to which the material in the intended application may be exposed. In addition to moisture and temperature, the effects of fuel, system fluids, NBC warfare agents and decontaminating media, paint strippers, and aging may cause deterioration in a composite structure. Suitable protection against or consideration of degradation of material properties must be provided for and demonstrated by test.

Susceptibility to Chemical Warfare Liquids

Resistance to chemical warfare liquids can be viewed as a specialized aspect of durability and solvent resistance peculiar to military material. These liquids fall into two categories, chemical agents and decontaminants, and each gives rise to its own set of concerns. For the toxic agents, the major worry is that a matrix material may absorb a quantity of the agent and, through diffusion, rerelease it at a time and place, such as a maintenance hanger, where its presence is not anticipated. The consequences for unprotected personnel could be devastating.

In the case of decontaminants, the concern is degradation of composite mechanical properties, both short- and long-term. This is especially true for the most common decontaminant, DS-2, an extremely caustic mixture of sodium hydroxide, diethylenetriamine, and methyl cellosolve. This aggressive fluid has already been shown to attack some plastics and elastomers. For instance, 24-hour immersion in DS-2 leads to the complete dissolution of a polycarbonate. Nylon takes up about 1 percent by weight, polyvinylchloride about 13 percent, polyethylene 0 percent, and a polyester loses 30 percent of its weight. In contrast, both glass- and graphite-reinforced epoxies showed only 0.4 percent uptake after 10 weeks of immersion. Kevlar-epoxy and glass-polyester composites showed 3.3 percent and 6.4 percent uptakes, respectively, over the same time span, an intermediate response. A similar wide range of behavior was seen in the uptake of stimulants of the major classes of agents. It is likely that thermoplastic matrix composites will exhibit a similar range of responses, depending on the chemical nature of matrix and the liquid. With DS-2, plasticization or bond scission or both are possible, as is attack at the resin-fiber interface. Indeed, with Kevlar and perhaps with glass, attack on the fiber itself must be considered. With regard to toxic agents, it is likely that some matrices will have an affinity for certain of them.

In view of this, it is evident that a necessary part of any evaluation of a thermoplastic composite for application to military material must include a screening for susceptibility to chemical warfare liquids. In those cases where adverse effects are noted, adequate protection can, in all likelihood, be provided by means of chemically resistant coatings currently available or under development.

THERMOSET MATRICES VERSUS THERMOPLASTIC MATRICES

Table 3-8 lists general properties associated with composites technology. In each category, the relative advantage of thermoset and thermoplastic matrix materials and aluminum metal is indicated. This section

TABLE 3-8 Matrix Comparisons

Property	Thermoset	Thermoplastic	Metal
Weight	+	+	
Material cost	+	+	+
Processing cost-reduction potential		+	
Simplicity of chemistry		+	
Melt flow	+		+
Prepreg tack and drape	+		
Long prepreg shelf life		+	
Low processing temperature	+		
Low processing pressure	+		
Low processing cycle time		+	
Low cure shrinkage		+	
Quality control data base	+		
Mechanical property data base	+		
Ability to translate fiber properties	+	+	
Solvent resistance	+		
Corrosion resistance	+	+	
Resilience	+		
Toughness		+	+
Lack of time-dependence	+		+
Interfacial adhesion	+		
Repairability			+
Low thermal expansion	+		

discusses many of these properties with emphasis on current needs and issues, which could form the basis for future research activity. Those properties associated with processing are treated in a separate section.

Weight

In comparing thermosets with thermoplastics, it is important to note that both these polymer families are quite attractive as matrices for minimizing the weight of the structures they form. Both classes of polymers are lighter than any metal or ceramic matrix, even on an absolute basis. Weight savings

for composites versus aluminum baseline are projected to be above 35 percent if reasonable design-allowable ultimate strains can be employed.

Costs

A cost comparison of fabrication methods for graphite/epoxy composites is shown in Figure 3-6. Obviously, the automated processes such as tape laying, filament winding, and pultrusion (not shown) are the most cost-effective. However, rapid processing does have its limitations as exemplified by the high void contents generally present in filament wound laminates. It can be assumed that graphite/thermoplastic composites will exhibit the same general cost trends shown in Figure 3-5.

Cost-wise, thermoset composites probably have a slight edge on the structural thermoplastic composites now in development (Table 3-9). One of the real attractions of thermoplastic matrix composites, however, is the potential for reasonably low processing costs. It should be noted that this

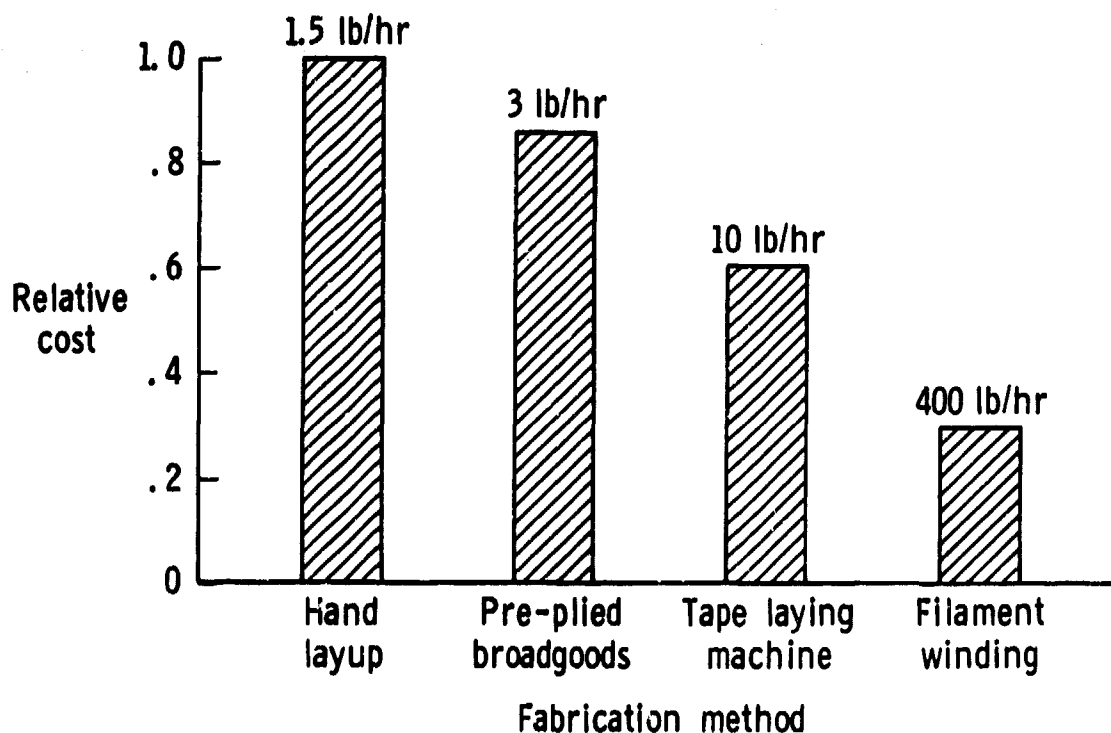


FIGURE 3-5 Cost comparison of fabrication methods for graphite/epoxy composites (Tenney and Dexter, 1985).

Table 3-9 Relative Costs of Thermoplastic and Thermoset Composites

Category	Thermoplastic	Thermoset
Raw Materials	more	less
Fabrication	same	same
Tooling	more	less

potential cost savings from innovative fabrication could be offset by higher material and tooling costs. Processing technology is discussed in more detail in Chapter 5.

Formulations

Epoxy formulations are generally very complex because of the large number of components involved: one or two base epoxies (often with a range of viscosities), curing agent(s), catalyst, and flow control agent. Thermoplastic formulations tend to be much simpler, often having only the basic thermoplastic (with some molecular weight control) or monomers in solution.

Semicrystalline thermoplastics offer a complicating feature: the presence of crystalline morphologies whose type and formation are influenced by process conditions, fiber surface, catalysts, etc., and which must be produced during the fabrication process. For such materials, there is a need to understand how changes in composite matrix morphology and degree of crystallinity affect composite properties. Specifically, with semicrystalline matrices, the desired morphology can be reproduced consistently during composite fabrication, regardless of part geometry and thickness (both of which affect heating and cooling rates).

Melt Flow

Epoxy formulations are oligomeric low-viscosity liquids that have high melt flow properties in the uncured state and, consequently, can penetrate fiber bundles and achieve good filament wetting during prepreg manufacture. Neat high-molecular-weight thermoplastics, on the other hand, may be prepregged either at high temperatures to achieve the appropriate low melt viscosity or in polar solvents that must later be removed. The dearth of melt viscosity/temperature relationships for high-performance resins to help guide prepreg and consolidation procedures points out a critical need for basic studies on the rheological behavior of these high-performance thermoplastic matrix resins.

The use of hybridized material forms to effect prepregging has recently been explored, whereby thermoplastic films or fibers are mixed with carbon fibers and the composite is formed by standard compression molding techniques. In this case, polymer flow patterns may be very different from those observed with standard coating techniques and may influence composite properties. This needs to be studied in some detail.

Powder impregnation is being developed for high molecular weight thermoplastics that preclude high temperature or solvent prepregging. The powder and comingled fiber preforms may provide a material that possesses the drape characteristics of a thermoset prepreg. However, the forming and consolidation steps are accomplished simultaneously with a volume change in the material.

In connection with the issue of melt flow is the challenge for the synthetic chemist to develop novel chemistry whereby tough, high T_g, high molecular weight thermoplastics can be made during the fabrication process by polymerizing low molecular weight, low-viscosity monomers or oligomers without evolution of volatiles.

The use of thermoplastic monomer precursors such as Avimid N and Avimid K-III requires sophisticated consolidation procedures during the molding process to effect both solvent removal, reaction products, and polymerization. Interestingly, 3-D weaves and preforms exacerbate the wetting problem both for epoxies and thermoplastics.

Prepreg Tack and Drape

While epoxy prepreg is formulated to have tack and drape, thermoplastic prepreg is boardy and tack-free, unless heat is applied or solvents are added that later react or volatilize. With PEEK and PPS, the use of solvents is not possible. Prepreg containing low-molecular-weight thermoplastic precursors has tack and drape because of the presence of a high-boiling solvent. Film and fiber hybrids and powder-coated tow have drape but no tack. The question remains, then, whether thermoplastic composites need to have tack and drape to be accepted in the aerospace market.

Prepreg Shelf Life

Most epoxy prepreps are formulated for a 2-week out life, defined as the working life under ambient conditions after removal from storage. Prepreps containing thermoplastic precursors also have a finite out life. In contrast, high-molecular-weight thermoplastic prepreg has an unlimited out life.

Quality Control

The quality and reproducibility of epoxy prepreg have improved greatly over the past few years. When handled properly, high-quality composite parts can be made consistently and with low scrappage. Thermoplastics have not reached this level of quality control. Problems exist with poor resin uniformity on the fiber, fiber wash, and excess void formation; these are to be expected in an emerging technology whose data base is extremely limited.

Mechanical Properties

Available data suggest no significant difference in 0° tensile properties between thermoplastic and thermoset composites. This would be expected, since such properties are mainly fiber-dominated. In compression, the situation is more complicated. Commonly used tests that measure hot and hot/wet 0° compressive strength probably are more a measure of a complex combination of properties rather than compressive properties alone. Whatever the mechanism of failure, it is generally found that 0° compressive tests indicate a superiority for thermosets, such as the standard 177°C cure epoxies, over thermoplastics. More data in this area are needed, as well as more detailed studies to indicate the nature of the failure in these tests. Another even more fundamental need is to understand what resin properties are required to efficiently translate the fiber properties to the composite.

In addition, it is not known whether it is universally critical for 0° compressive strengths of thermoplastic composites to equal those of standard epoxies. If it is critical, how can this goal be achieved? For instance, would this achievement require improved resins, improved fibers, or improved resin-fiber interaction? Furthermore, if this goal cannot be achieved, can equally satisfactory products be produced by changing the design?

It needs to be emphasized that matrices for advanced high-performance composites must have an acceptable balance of properties: hot and hot/wet mechanicals, residual mechanicals after damage, interlaminar fracture toughness, creep and fatigue resistance under a variety of environmental conditions, resistance to microcracking, cost-effective processing, and thermal stability. One property cannot be ignored in the process of trying to improve another. The relationship between resin tensile modulus and composite interlaminar fracture toughness, G_{Ic} (Figure 3-6), illustrates the trade-offs that must be considered, although the general trend seems to be more valid for thermosets than for thermoplastics.

Solvent Resistance

Many of the early standard thermoplastics, such as polyethylene, polystyrene, and polycarbonate, had relatively poor resistance to solvents and aggressive fluids. However, a large number of high-performance thermoplastics are quite impervious to standard soak tests (Table 3-5).

These questions relating to solvents need to be addressed:

- How can solvent sensitivity be characterized under load? For long times?

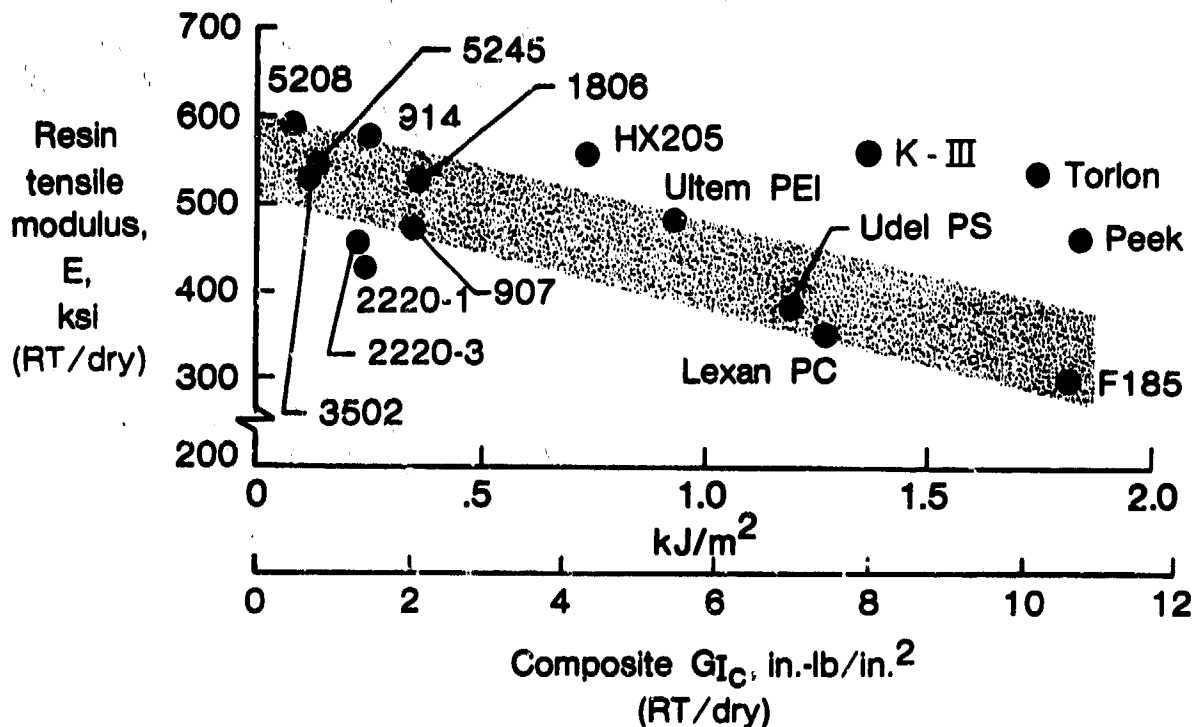


FIGURE 3-6 Resin modulus versus composite interlaminar fracture toughness (Johnston, 1984).

- Can a proper balance be obtained in thermoplastics between solvent resistance, toughness, and ease of processing?
- Does the need to screen thermoplastic composites for chemical warfare liquid susceptibility constitute a significant barrier to their use in military material?

Fracture Toughness and Resilience

The data in Table 3-7 demonstrate that thermoplastic composites perform much better than the standard brittle epoxy composites in fracture toughness and impact tests. However, some issues remain:

- What is a reasonable interlaminar fracture toughness goal, in terms of mode I, mode II, and mixed-mode test results (as defined in fracture mechanics) for highly loaded structural applications?
- What is the influence of temperature, load rate, and moisture on interlaminar fracture toughness values?

A better understanding of deformation mechanisms in the thermoplastic matrix is also needed so that preferred energy-absorbing deformation modes can be encouraged and others inhibited. It is not clear whether "toughness" mechanisms can effectively operate in the constrictive zone between fibers.

Because of the nonlinear stress-strain behavior of thermoplastics, much of their toughness is obtained from irreversible deformation mechanisms such as plasticity. The amount of toughness stored in a linear elastic reversible manner is defined as the resilience, and researchers must begin to measure and compare resilience values to define the use limits of the respective matrix materials. This should be done in compression and shear loadings as well as in tension. In this connection, the questions should be answered: Can linear elastic fracture mechanics help explain fracture in thermoplastics? Or will nonlinear treatments be required?

As mentioned in a previous section, the post-impact compression test is an important damage-tolerance test for composite materials. From the limited data in Table 3-7, thermoplastic matrices seem to do well; a first-generation epoxy composite such as 3501-6/AS-4 does not. The test has been studied extensively on first- and second-generation epoxy composites.

Correlations between post-impact compressive strength and G_{IC} values for a select number of materials (Figure 3-7) indicate a dependency of the former on interlaminar G_{IC} values up to about 3 in.-lb/in.² (525 J/m²). Correlations between post-impact compressive strength and other resin and composite properties are needed to provide more economical and faster screening tests for damage tolerance.

Nonlinear and Time-Dependent Behavior

Although all polymeric materials exhibit nonlinear stress-strain behavior and time-dependent response, this behavior is not very significant in brittle thermoset resins in normal use. It is well known that thermoplastic resins exhibit significant nonlinear stress-strain behavior, and this behavior must

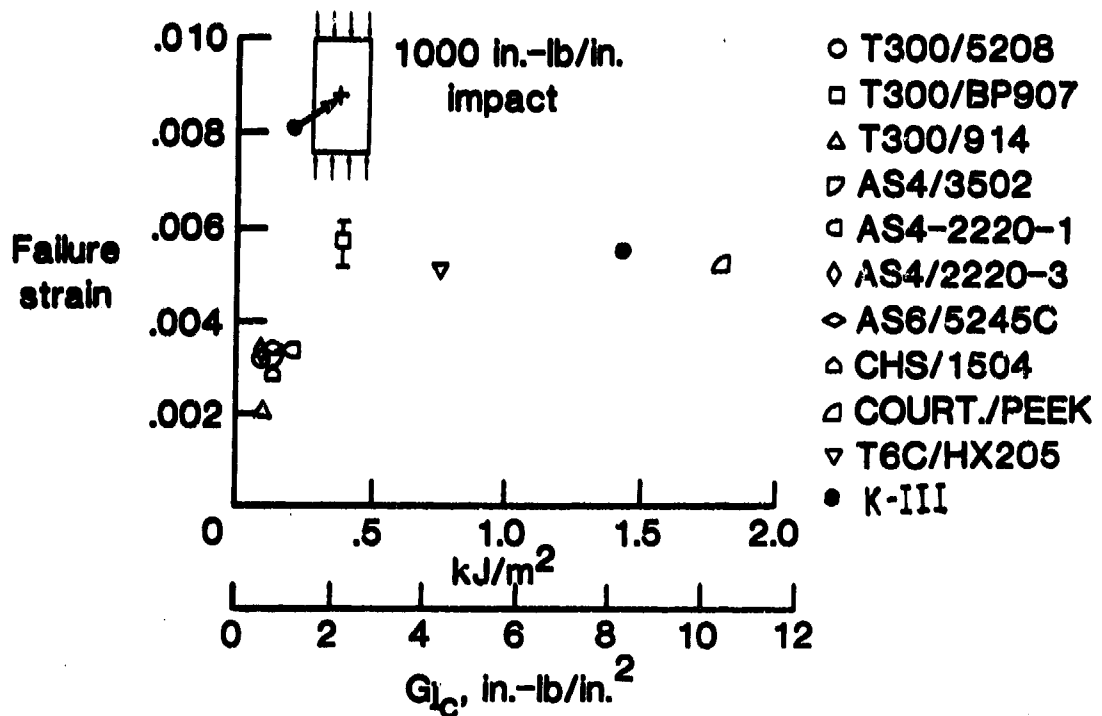


FIGURE 3-7 Compression after impact failure strain versus fracture toughness (Williams et al., 1984).

be accounted for in design. Very little data is now available, but it is suspected that the time-dependent behavior of thermoplastic composites will be no better (and possibly worse) than that of thermoset composites.

The fatigue data plotted in Figure 3-8 was obtained from cycling ($\pm 35/0/90$)_s specimens at various strains less than that required for edge delamination ($R = 0.2$, $f = 10$ Hz) until delamination initiated at an edge. In all cases, fracture toughness decreased with increasing cycles. However, it can be seen that under these rather severe conditions the thermoplastic composite (PEEK APC-2) has poorer fatigue resistance than the toughened epoxies (H205 and HST-7), which are poorer than the brittle 5208 epoxy.

The following issues need to be addressed:

- Can thermoplastic composites perform well in fatigue? In long-term creep under hot and wet conditions?
- If not, can the matrices be tailored to allow acceptable composite fatigue performance without unduly compromising other properties?

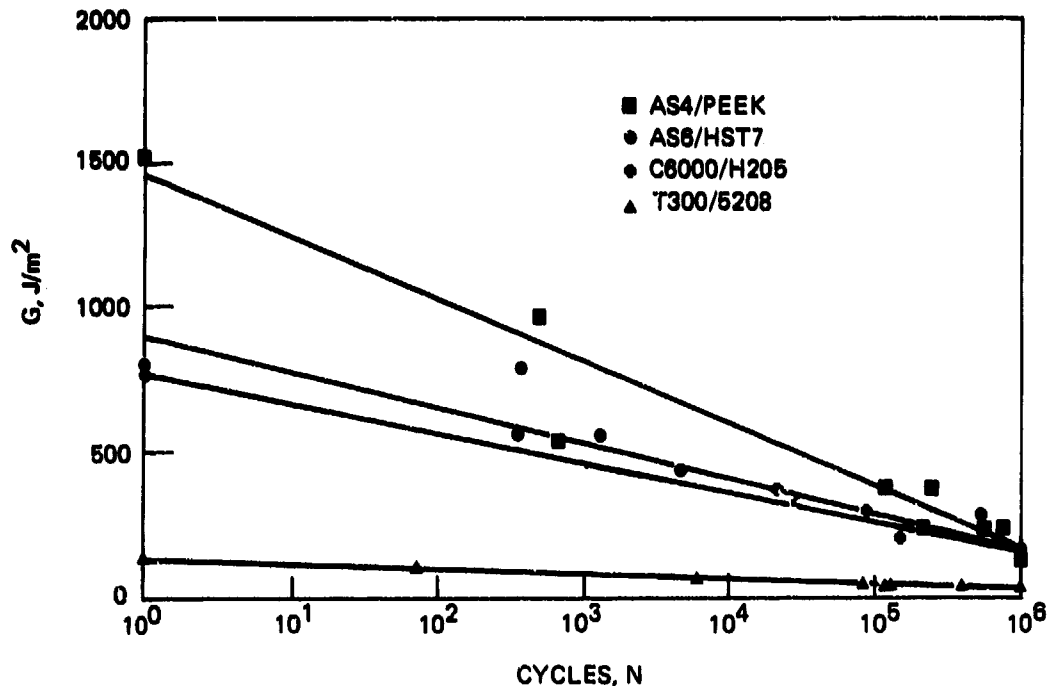


FIGURE 3-8 Interlaminar fracture toughness as a function of fatigue cycles (O'Brien, 1986).

- Can composite creep be controlled by the type of carbon fiber employed or by interfacial treatments?
- Can an acceptable simple compression creep test be developed as a screening tool for new thermoplastic matrix candidates?

It is obvious that this is fertile ground for much-needed experimentation. Responses to the fatigue environment, including hysteresis heating and crack propagation phenomena, also need to be carefully studied.

Environmental Aging

Thermosetting composite materials chemically cure to a highly cross-linked, three-dimensional polymer network structure. It is the nature of such materials to be reasonably solvent and creep-resistant over the environmental conditions to which common military and civilian aircraft are exposed. Twenty years of experience with these materials, coupled with glass-reinforced composite experience dating back to World War II, provide a basis for environmentally resistant structures. Thermoplastic composites must now be evaluated through carefully planned and executed environmental tests to address these concerns. Accelerated testing must reliably predict the effects of the real-time environment and the interaction of variables (e.g., load, moisture, and temperature).

Other questions concerning environmental aging are these:

- What properties are required for 60,000 hour durability?
- With semicrystalline thermoplastic composites, is percent crystallinity constant with time under load? Is it constant with time in the presence of aggressive liquids such as hydraulic fluids or methylene chloride.
- For thermoplastic composites in general, what aging mechanisms will be significant?
- Can long-term durability be assured by quality control and nondestructive investigation techniques?

The problem of aging under load is severe for bulk thermoplastics. Annealing and the insertion of rigid molecular moieties in the polymer chain help. Research should be conducted to try to correlate crazing and aging embrittlement in bulk materials with composite properties related to aging. Also, the effect of moderate steady and cyclic shear stresses on time to failure should be investigated. Because the stress loading is very different in composites compared to bulk polymers, the aging could be very different.

Residual Thermal Stresses

One of the major issues with thermoplastic matrix composites is the potential thermal stresses resulting from the great differences in thermal expansion properties of the fibers and matrices.

For amorphous thermoplastics, a large thermal property mismatch between graphite or Kevlar aramid fibers and typical amorphous thermoplastic matrices can lead to large residual stresses. In processing amorphous thermoplastics, the stresses build up after the material drops below the glass-transition temperature, therefore, the build-up is likely to be insensitive to typical processing conditions.

The mechanism of stress build-up with semicrystalline thermoplastic matrices may be complex and dependent on processing conditions. If the semi-crystalline matrix assumes enough solid-like character early in the crystallization event, the constrained shrinkage will be large, resulting in large residual stresses or cracking. If stress does not build up until after the crystallization is nearly complete, the stresses will be smaller, but dimensional changes may be significant.

Interfacial Adhesion

A major concern involving the use of thermoplastics as matrices on carbon fiber is the fact that fiber-resin interfacial adhesion exhibited by such materials as PPS (IV), polyetherimide (IX), polysulfones (XVI), and polycarbonate is less than that observed for epoxies. For example, it is

easily seen from the photomicrographs in Figure 3-9 (site B) that bare fibers dominate the 30° - 90° interface delamination surface in a Udel P1700/T300 edge delamination (+ or - 30° , + or - 30° , 90° , 90°) specimen. The T300 fibers contained a standard epoxy size, and this size was not optimized for thermoplastics. This is representative of what is observed on fractured surfaces of edge delamination and double-cantilevered beam specimens made from the other materials.

Also, from Figure 3-4, it can be seen that the data points for three thermoplastics fall well below the dotted line connecting the thermoset data points. Although not identified on the figure, these three data points are for polymers Ultem 1000 (IX), P1700 polysulfone (XVI), and polycarbonate. Apparently, in these cases, the interfacial adhesion is lower than the load required for a cohesive failure in the matrix.

It is not well understood how or why a good fiber-resin interface is attained even with epoxies. It is obvious that basic understanding of

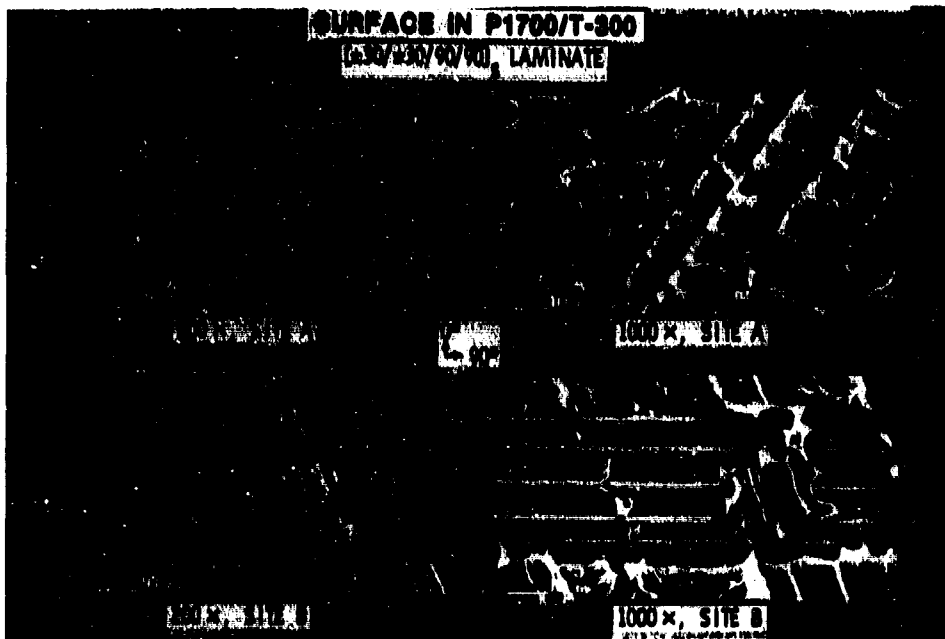


FIGURE 3-9 SEM photomicrographs of 30° - 90° interface delamination surface in P1700/T300 specimen.

interfacial adhesion between carbon fiber and resin matrices, especially thermoplastic matrices, needs to be improved. These questions need to be answered:

- How can the tensile and shear properties of a fiber thermoplastic resin interface be measured?
- What interface properties are important? Can a successful model for the interface be developed that will help guide exploratory research?

- How can the adhesion of the matrix to carbon fiber surfaces be improved? Can the interfacial adhesion properties be systematically tailored?
- What is the role of the interface and interphase in controlling toughness, mechanical, and durability properties of composites?

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Chapter 4

SHORT-FIBER-REINFORCED COMPOSITES

Thermoplastics containing short-fiber reinforcement were first introduced into the marketplace some 25 years ago. These materials represented a new range of performance capabilities and were designed to fill the property gap between high-volume commodity plastics and sophisticated continuous-fiber reinforced composites. Enhancements of properties (e.g., strength, stiffness) resulting from short-fiber reinforcement are relatively modest compared to the properties of the parent thermoplastic resin and certainly fall far short of the continuous-fiber reinforced composites. Nevertheless, these short-fiber-reinforced thermoplastic materials have found and continue to find their way into lightly loaded secondary structures and engineering applications where the unreinforced parent resins will not perform satisfactorily. A more detailed treatment of short-fiber-reinforced composites is given in Appendix C.

General criteria for considering the use of these materials are these:

1. Applications requiring moderate loading--up to 30,000 psi tensile; up to 30,000 psi flexural strength.
2. Applications requiring moderate stiffness--up to 2×10^6 psi modulus.
3. Applications where toughness requirements are critical.
4. Applications involving high-volume production.
5. Production of parts containing complex three-dimensional geometry.
6. Applications where long shelf life and scrap recycling are important issues.
7. Applications where potential exists for hybrid parts containing high-strength laminate skins.
8. Applications where field repairability via melt fusion is important.

In recent years new, high-temperature thermoplastic resins, commonly called engineering resins, have emerged, and the combination of these resins with a variety of short-fiber reinforcement including glass, carbon, and aramid fibers has significantly broadened the performance capabilities of

short-fiber reinforced systems. The effect of these fiber reinforcements on a broad range of properties of the base resin is expressed in general terms in Table 4-1. More detailed information on glass- and carbon-fiber reinforcement of engineering thermoplastics is given in Table 4-2. Although this information admittedly is a grossly simplified presentation of the effect of short-fiber reinforcement and concomitant performance capabilities, it does define broad limits for design considerations. Certainly a number of other factors such as fiber alignment, aspect ratio, fiber-matrix interface, processing parameters, and time-dependent behavior play an important role in individual part performance. These factors are discussed in greater detail in the appendixes of this report.

Possibly the greatest virtue of short-fiber reinforced thermoplastics is their ease of processing. This has been and continues to be a major driving force to their widespread use. Thermoplastics containing short-fiber reinforcement can be molded quickly and reproducibly by a variety of convenient processing techniques (see Appendix C for details). This fast processing and the ability to produce extremely complicated and detailed parts have been the keys to successful competition with comparable thermoset

TABLE 4-1 Effect of Short-Fiber Reinforcement on Engineering Thermoplastic Resins

Property	Glass	Carbon	Aramid
Typical loading level, wt %	10 to 50	10 to 40	5 to 20
Tensile strength	Significant effect	Very large effect	Some effect
Flexural modulus	Significant effect	Very large effect	Some effect
Impact strength	Some effect	Moderate decrease	Some effect
Heat distortion temperature	Very large effect	Moderate to very large effect*	Very large effect
Flame resistance	Some effect	Some effect	Negligible effect
Electrical conductivity	No effect	Very large effect	No effect
Wear resistance	Some effect	Very large effect	Some effect
Chemical resistance	Significant effect	Very large effect	Some effect
Dimensional stability	Significant effect	Very large effect	Some effect
Molding precision	Some effect	Some effect	Significant effect
Creep resistance	Significant effect	Very large effect	Some effect

*Heat distortion temperatures are dramatically increased in semicrystalline resins and moderately increased in amorphous resins.

TABLE 4-2 Effect of Short-Fiber Reinforcement of Engineering Thermoplastic Resins

	Tensile Strength, 10 ³ psi	Flexural Modulus, 10 ⁶ psi	Unnotched Impact, ft-lb/in.	Heat Deflection Temperature, °F
Amorphous thermoplastics				
Base resin	8 to 15	0.3 to 0.4	25, no break	250 to 400
30% glass fiber	20 to 30	1.1 to 1.5	7 to 15	285 to 425
30% carbon fiber	30 to 35	1.7 to 2.3	6 to 13	290 to 425
Crystalline thermoplastics				
Base resin	10 to 15	0.4 to 0.6	3.5 to >40	200 to 400
30% glass fiber	20 to 30	1.3 to 1.8	5 to 20	~500
30% carbon fiber	25 to 40	2 to 3	5 to 12	~500

materials and metals. The ease of processing (i.e., the ability to form parts in multicavity molds in extremely short cycles) and the ability to recycle scrap also offer the potential for significant cost reductions compared to thermoset compounds and metals. Thus, short-fiber reinforced engineering thermoplastics have established themselves in the electrical and electronics, automotive, oilfield, chemical process, and defense industries and are now successfully penetrating the engineering applications (e.g., aircraft, aerospace) where load-bearing requirements are important.

Still, the mechanical properties of many short-fiber reinforced thermoplastics fall well short of their theoretical values. Although this has not been a major drawback in the past, it is certain that improvements in fabrication and optimization of properties will be required if these materials are to be considered, either alone or in combination with long-fiber composites, for critical load-bearing applications. The increasing need for high specific strength and stiffness, coupled with high-temperature environments, requires that the reinforcing effect of the fibers be used to maximum benefit. These requirements mandate an appropriate understanding and the ability to control the effects of processing parameters on microstructure, fiber alignment, fiber length, etc. The need for computer programs (CAD, CAM) for both design stresses and mold flow prediction is increasing. Implementation of a three-dimensional viscoelastic constitutive equation to accurately describe the nonsteady-state, nonisothermal flow behavior of filled polymer melts is essential. The use of finite-element analysis as an aid to part design is likewise essential.

In conclusion, short-fiber reinforced thermoplastics have come a long way in the past 25 years. They have been successful in partially bridging the gap between commodity resins and sophisticated long fiber composites and now enjoy

a multimillion-pound annual market. Further refinement of compounding and processing technology coupled with improvement in reinforcement and part design technology could allow the performance window for these materials to be broadened considerably. For example, the fiber length in traditional short fiber composites is approximately 1/8 in. or less. The following general conclusions are appropriate to that class of materials:

- Short-fiber reinforced thermoplastic composites generally do not meet design specifications for primary load-bearing applications.
- These composites can be used very cost effectively in a number of secondary load-bearing and conventional applications.
- Short-fiber thermoplastic composites offer processing advantages over comparable thermosetting systems.
- State-of-the-art processing technology does not allow control of fiber length or orientation distributions. Accordingly, properties usually fall short of theoretically achievable values.
- Rheological behavior of fiber-filled melts is not sufficiently understood.
- Short-fiber thermoplastic composites offer increased toughness compared to state-of-the-art thermosetting systems.
- Innovation in manufacturing methods that result in greater fiber length can be expected to increase material strength and toughness.

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Chapter 5

PROCESSING

The thermoplastic nature of the resin matrix allows fiber-reinforced thermoplastic composites to be processed by a variety of techniques. Although each of these techniques is distinctly different from the others, they all involve a series of common sequential steps:

- Heating composite to form mobile liquid form (i.e., melt)
- Forming part from composite melt
- Cooling part to temperature below solidification point
- Removing formed part from mold

These processing techniques often use thermoplastic polymer pre-impregnated fabric, tape, or tow precursors. Alternative approaches combine the reinforcing fiber with the thermoplastic polymer during the molding process. In either case, combination of the reinforcing fiber with thermoplastic polymer is based on hot-melt technology or solution coating. Thus, what follows is a discussion of composites based on thermoplastic melts and solution coatings.

The most common molding techniques are summarized in Appendix A. Some selected examples of long-fiber reinforced thermoplastic composite part fabrication are listed in Appendix B.

COMPOSITES BASED ON CONVENTIONAL THERMOPLASTIC MELTS

The most commonly employed method of introducing reinforcing fibers such as aramid, glass, and graphite or carbon has been to melt the thermoplastic directly with the reinforcing fibers to make the thermoplastic tape or tow. Examples of this are ICI's APC-2 (carbon fiber-polyetheretherketone) and Phillips Petroleum's carbon fiber-"Ryton" (polyphenylene sulfide). In such products there is generally excellent fiber wet-out with a low void content. The melt-impregnated tape or tow serves as the raw material for composite part fabrication. A series of plies are oriented properly and consolidated to produce a finished part. Flat sheet stock produced in this manner can subsequently be postformed by a variety of methods to achieve complex shapes.

Compression molding has been the most commonly used fabrication technique to date. In the long term, a consolidation process that involves automated tape or tow laydown is desirable. The potential advantages of such an automated process are significant. Rigid, nontacky thermoplastic tapes or tows are normally difficult to control in manual operations. With the entire process automated, labor costs should be reduced. In principle, there should not be a need for additional processing steps.

A critical examination of the automated laydown process reveals many unresolved issues:

- Can automated processes be developed that produce thermoplastic laminates with the quality required?
- Is it possible to eliminate gaps? With thermosetting systems the resin melt viscosity during the early stages of cure is normally low enough to allow for complete gap filling. This would be unlikely in the case of the thermoplastics because of the relatively high melt viscosities that are involved.
- Will edge fusion be required?
- Can misaligned tapes be removed and reapplied? In thermosetting systems, misaligned tapes can be easily removed and repositioned manually.
- Can economical production rates be achieved?

Film or Powder Stacking and Powder Coating

A convenient and potentially less expensive procedure for preparing a thermoplastic composite part is to use the film or powder stacking procedure. This procedure works best with the reinforcement in the fabric form. Layers of the fabric are interspersed with layers of thermoplastic film or powder. Compression or autoclave molding causes the thermoplastic to wet the fibers and form the matrix. This procedure requires relatively severe conditions (elevated temperature and pressure) to achieve a low-void laminate. It does, however, have the advantage that curved tool surfaces can be employed with relative ease.

Powder coating offers unique and, in some respects, revolutionary processing techniques for the preparation of high performance prepreps. Recent unpublished work (J. H. Hartness, BASF Structural Materials, Inc., 1987; J. Muzzy, Georgia Institute of Technology, 1987; and D. D. Edie, Clemson University, 1987) has shown that high quality carbon fiber impregnated tow and tape can be prepared from powder of thermoplastics and thermosets without the use of heat or solvent. These procedures utilize flurry, fluidized bed, and electrodeposition techniques and powder sizes ranging from 2 to 50 μm in diameter. The prepreps have good drape and, in some cases, good tack through the use of a fugitive tackifier. Further work is required to determine if impregnated tow can be woven, pultruded, or filament wound. The major disadvantage of this approach is the high cost associated with the preparation from tough thermoplastics of powders having reasonably

small particle sizes. Powder coating techniques offer a potential breakthrough in thermoplastic prepreg fabrication that deserve further exploitation.

Flexible Thermoplastic and Reinforcing Fiber Hybrids

Comingling of thermoplastic fibers with reinforcing fibers is an interesting and innovative means of combining the thermoplastic with reinforcing fibers. Co-woven hybrid fabrics can be prepared by weaving the infusible reinforcing fibers with either spun thermoplastic fibers or narrow widths of slit film. The hybrid fabric has great flexibility and can be easily formed to a curved tool surface and consolidated with heat and pressure. In the molding process the thermoplastic fibers or slit film melt and flow together and wet the fibers to form the resin matrix for the composite part.

Some critical questions pertaining to these processes remain:

- Are the processes economical?
- What are the practical size limitations?
- What fiber volumes and distributions can be achieved?
- Can good fiber wet-out be achieved?
- Can low-void parts be fabricated?
- Are new reinforcing-fiber surface treatments required?

COMPOSITES BASED ON SOLUTION COATED THERMOPLASTIC PREPREGS

Certain amorphous thermoplastics possess sufficient solubility in organic solvents to allow for dip-coat, "B"-stage prepegging. A degree of tack and drape can be attained if some of the solvent is left in the prepreg. The critical issue related to these materials is whether low-void laminates can be fabricated. If the prepreg is completely devolatilized, a conventional boardy and nontacky thermoplastic tape or fabric is obtained. Processing devolatilized thermoplastics is similar to hot-melt processing.

Examples of polymers that fall into this category, together with the typical impregnation solvents, are "Udel" P-1700 polysulfone (methylene chloride), "Torlon" polyimide imide (N-methyl-2-pyrrolidone), and "Ultem" polyetherimide (N-methyl-2-pyrrolidone).

COMPOSITES BASED ON "THERMOSETTING" THERMOPLASTICS

Certain polyimides, by virtue of their unique monomer combinations, possess true thermoplastic properties. Although it is possible to make thermoplastic polyimides that can be processed using conventional thermoplastic processing techniques, it is also possible to take advantage of well-known polyimide chemistry and prepare the thermoplastic polyimide *in situ* on the reinforcing fibers from monomeric solutions. The versatility of the "thermosetting" thermoplastic polyimide approach to composite processing is illustrated in Figure 5-1.

Processing of Prepreg-Containing Volatiles

A good example of a thermosetting thermoplastic polyimide is DuPont's "Avimid" K-III polyimide. In this case the binder solution consists of a mixture of an aromatic diamine and an aromatic diethyl ester diacid dissolved in a solvent (N-methyl-2-pyrrolidone). Essentially monomeric solutions with high solids and low viscosity can be prepared and used in the preparation of prepreg using the same techniques that have been used for many years with epoxies. These include both pseudo-hot-melt as well as dip-coat, "B"-stage preprepping. Such prepreg can possess good tack and drape at room temperature. Consolidation is effected in an autoclave or press. Although the pressures (100 to 200 psi) and heat-up rates (1 to 2°C/min) are similar to those employed with epoxies, there are two major differences: the processing temperatures are higher (343°C for K-III versus 177°C for epoxies), and volatiles (water, ethyl alcohol, and N-methyl-2-pyrrolidone) are evolved over the course of cure. A major concern with any material that evolves volatiles during processing is the formation of voids. In the case of K-III, a well-defined glass transition temperature (250°C) exists, offering a mechanism for the elimination of these voids. The application of pressure above the glass transition temperature provides a means to eliminate voids. In fact, the autoclave processing of Avimid K-III laminates has been amply demonstrated. Large area parts have been successfully fabricated. Both thin and thick laminates have been cured simultaneously. In all cases the void content is less than 0.5 percent.

The critical issue is whether thick, low-void laminates can be made in spite of the volatiles. From the flow sheet in Figure 5-1 it can be seen that, in dealing with prepreg-containing volatiles, there are a variety of ways in which parts can be fabricated. Prepreg tape not only can be laid up by hand but also should be capable of automated laydown using the same equipment and conditions as currently employed with epoxy prepreg tape. The problem of gaps described previously in the laydown of conventional thermoplastic tapes might be resolved--e.g., a misaligned tape could be easily removed and repositioned by hand; there may be enough flow in the system in the early stages of cure to fill in the gaps between tapes; there should be no need to blanket the laydown point with inert gas to prevent undesirable oxidative side reactions, since the laydown process could be carried out at room temperature.

In addition to automated tape laydown possibilities, filament winding using either a wet winding process or prepreg tows should be possible.

Processing of Precured "Thermosetting" Thermoplastic Polyimide Prepregs

The possibility exists that "thermosetting" thermoplastic polyimide tapes are capable of being devolatilized (consolidated) under carefully controlled conditions and eventually processed much like the conventional thermoplastic versions.

In addition to devolatilized tapes, devolatilized fabric prepreg is yet another product form that could be autoclave- or press-molded to the finished

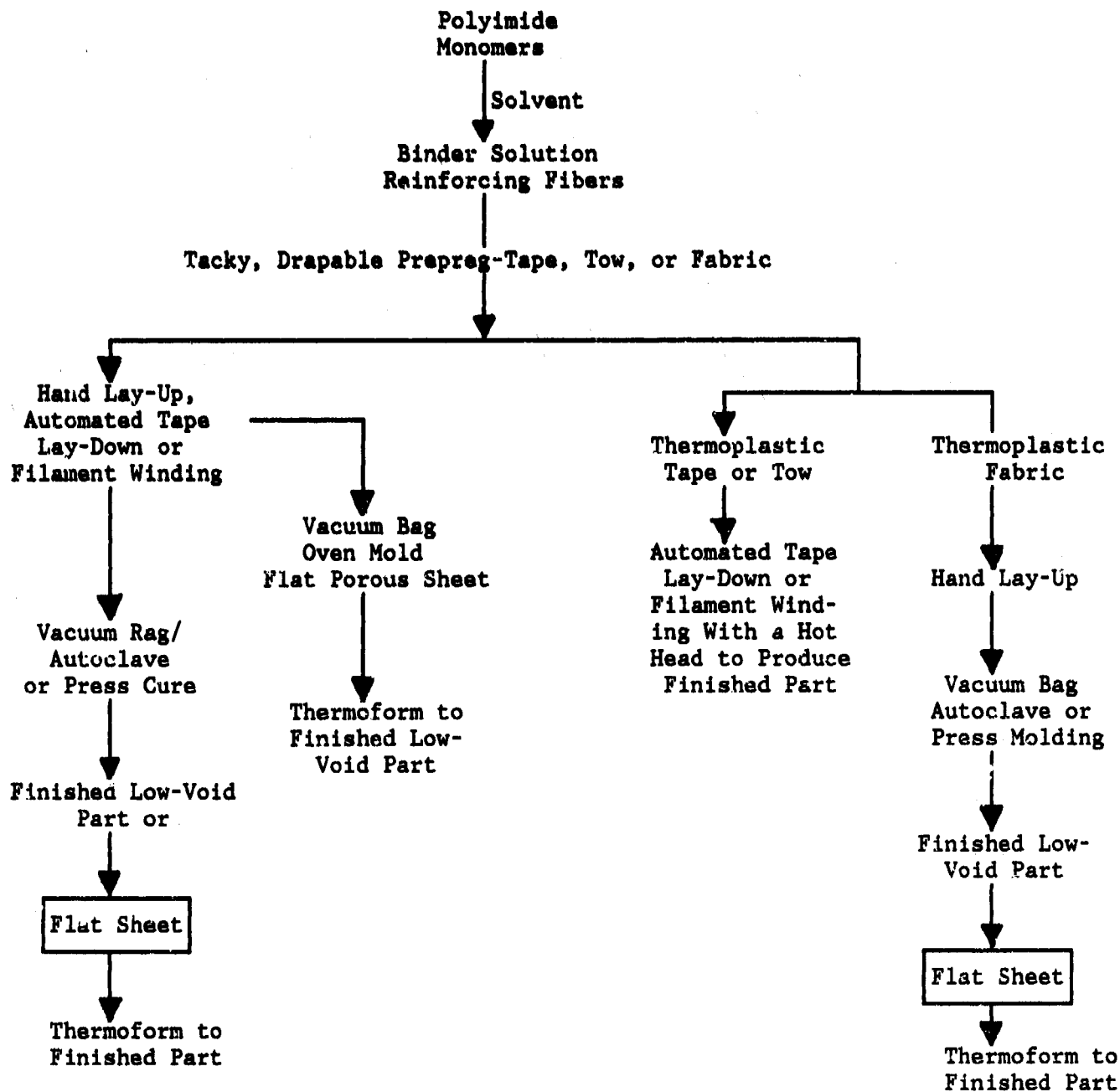


FIGURE 5-1 Thermosetting thermoplastic polyimide composite processing.

low-void part. Flat sheets could also be produced with tape or fabric prepreg for thermoforming.

SURFACE TREATMENTS OF REINFORCEMENTS

Another major concern involving thermoplastic matrix composites is the issue of surface treatments for the reinforcements. Although little or no studies have been completed on the effects of treatments on fibers for thermoplastic matrix composites, it would be of value to review the technology as it has applied to thermosets, inasmuch as the considerations concerning approach and effect are often the same. Several factors are usually considered concerning the choice and application of surface treatments to fibers. One concern is to enhance further processing and handling, and the other is the desire for enhancement of the bond between the surface of the fiber and the resin matrix.

The issue of surface treatment choice is complex, in that one must consider in detail the nature of the thermoplastic with which one is working. The choices involve amorphous polymers, such as polysulfone; semicrystalline polymers, such as a polyetheretherketone; reactive polymers, such as a polyimide; and a liquid crystal polyester, such as Xydar. Each family of resins will have to be considered individually because the choice of fiber treatment must be tailored on the basis of many factors. Another major consideration to be addressed is the nature of the reinforcement. The nature of the surface treatment will be determined by whether one is looking into carbon-graphite fibers, glass, or organic reinforcement, such as Kevlar.

Although extensive work has been reported in the literature regarding surface treatments for graphite and glass fibers, it has been directed for the most part to thermosets.

One of many issues that must be addressed when considering a surface treatment, especially if the treatment is an applied sizing or finish, is determining the processing conditions that the composite must undergo that will result in a high-quality laminate. In the case of the amorphous, semicrystalline, and liquid-crystalline thermoplastics, the materials are usually taken above the melt of the polymer and held there for some time to achieve good wetting and consolidation. These temperatures often run as high as 380°C, which is obviously much higher than any epoxy sizing could endure. This challenges one to design a sizing that is thermally stable, bonds well to the fiber, and is compatible with the matrix of choice. In addition, one must have a sizing that is easy to apply and results in improved composite properties. In the case of the reactive thermoplastic polyimides, one must again consider temperatures often as high as 350°C for 3 hours and the possibility that reaction may take place between the polyimide and the fiber coating.

Hartness reported on work (Husman and Hartness, 1979; Hartness 1980 and 1982) in which films of polyphenyl sulfone, polyphenylene sulfide, and polyetheretherketone were individually stacked with graphite cloth sized in one case with epoxy and with an amorphous thermoplastic, phenoxyl, in the other. It was noted that in all cases the thermoplastic phenoxyl-sized graphite cloth wetted out much better, whereas the epoxy-sized graphite

resulted in poor wet-out and voids inside the fiber bundle. It was speculated that the phenoxy acted as a lubricant or interpenetrating polymer network (IPN). The processing temperature for these thermoplastics is much too high for the epoxy sizing, and this probably resulted in its thermal degradation, also causing an unfavorable surface on the graphite for bonding. Some users of the film-stacking technique have elected to thermally remove the epoxy sizing prior to film stacking, thus leaving the graphite fiber surface clean (Air Force Wright Aeronautical Laboratory, 1984). Results from this technique have resulted in good wet-out when stacking polyetheretherketone film with graphite cloth. The film-stacking technique challenges the effective use of a coating, in that the polymer is required to melt from the outside of the ply and effectively wet-out the interior of the fiber bundle. This is in contrast to a prepreg product, in which the polymer is in intimate contact with the fiber prior to consolidation.

It has been speculated that, in the case of the unreactive thermoplastics, little or no reaction will take place with a sizing on the reinforcement. In the case of the reactive polyimides, reaction with a specific coating may offer more prospects for good adhesion.

As has been pointed out by others, the role of silane coupling agents for enhancing the bond of resin matrixes to glass fibers has much documentation. Plueddemann's (1982) work on the subject has been thorough and offers a good background. Plueddemann offers a number of possible routes to bonding thermoplastics to glass. In the first case, bonding through chemical reaction is possible for those thermoplastics that contain functional groups such as amides, esters, carboxyls, hydroxyls, or halides that could react quite readily with other organofunctional groups at molding temperatures. Plueddemann holds out the possibility for grafting reactions for the nonreactive thermoplastics.

The next area is bonding through solution compatibility or diffusion. It is pointed out that, in those cases where no reaction is possible, a definite maximum in laminate properties is obtained with silanes that have optimum compatibility with the polymer, as predicted from solubility parameters of the organofunctional silane and the resin. Coupling through solution compatibility is most successful with glassy polymers like polystyrene but less effective with crystallizing polymers like polyethylene or polypropylene.

The last suggested mechanism for bonding is through interpenetrating networks. Plueddemann points out that certain reactive silanes with amine, methylacrylate, or cationic vinyl benzyl functions often perform very well as coupling agents in thermoplastic composites, even though there is no obvious reaction or preferred solubility of the silane and the polymer. It is pointed out that establishing a strong interpenetrating boundary layer involves a complex interplay of mechanical and chemical activities at the interface. Whether the adhesion promoter is applied as a primer or is used as an integral additive, it must have partial compatibility with the matrix resin in order to establish an interpenetrating network structure. If it is too compatible (soluble), it will lose its identity by dispersing into the top coat. If it is too incompatible, the top coat will not establish a bond with it.

Improved adhesion across the interface is generally accompanied by improved mechanical properties and water resistance in the composites. It has been pointed out from several sources that it may be necessary to attain a compromise in interface properties of adhesion, because fracture toughness in glass composites may be decreased by improved adhesion; hence, the coupling agent may require chemical modification to accommodate the toughness (which requires a weaker adhesion at the interface) with the good adhesion required for maximum strength. How this reasoning applies to a tough thermoplastic matrix that is less prone to delaminate is unclear.

Finishes and coupling agents designed for organic fibers such as Kevlar must take into consideration the thermal stability of the reinforcement and if that consideration can be satisfied, then the possibility of designing coupling agents that would be successful seems possible.

SEMICRYSTALLINE MATRIX COMPOSITES

Morphology-Property Relationships

One of the fundamental issues affecting semicrystalline thermoplastic matrix composites is the influence of morphology on the properties of the composite. Changes in polymer morphology may occur as a function of composite processing. One of the unique features of thermoplastic composites is the ability to process at various heating and cooling rates. This is due to the absence of the exotherm experienced in the case of thermosets. One must consider the extremes in processing temperatures that may be encountered in the aerospace industry. These extremes may be encountered from the fabrication of thin parts where rapid cooling may occur, to parts many inches thick, to a thermoforming operation or to a processing condition in which a tapered thickness part may be encountered.

Polymer morphology is primarily the study of order within macromolecular solids. This ordering occurs at a variety of sizes, from interatomic to macroscopic. The aspect of polymer morphology most likely to be met with, because it is so widespread and can be seen in an optical microscope, is spherulitic ordering (i.e., spherulites in various stages of development).

In addition to spherulitic ordering, one must address the order within the spherulite, which is composed of lamella. Within the lamella one studies crystal structure (i.e., chain packing), using x-ray crystallography. Although the neat resin morphology has been studied in detail, description of the polymer matrix in composites has concentrated on the spherulitic structure. One would hope that the concepts developed for pure polymers would help in understanding how changes in composite matrix morphology affect composite properties.

The few studies in the area of morphology and property relationships for a particular semicrystalline matrix material, polyetheretherketone, show little relationship between spherulite morphology and composite properties.

At this point one must look at each individual system. The two semicrystalline polymers used as matrix materials are polyetheretherketone and polyphenylenesulfide. These materials are addressed here as they perform as matrix material and not as neat resins.

Polyetheretherketone

There are two major forms for polyetheretherketone (PEEK) in a composite. The first is the Imperial Chemical Industries' (ICI) prepreg product, APC-2. The other is the various combinations resulting from PEEK resin in the form of film or spun fiber combined with graphite, glass, or Kevlar fiber by film stacking, or comingling in the case of the PEEK filaments. The two types of treatment arise because of differences in polymer melt viscosity and molecular weight. Both of these parameters affect polymer morphology. It is expected that additional product forms will be developed.

The prepreg product, APC-2, has been most investigated and consists of PEEK polymer tailored for prepping by ICI, combined with Hercules' graphite fiber AS-4. The fiber-volume is approximately 60 percent. The effect on morphology-property relationships for a 60 percent fiber volume is significant in that the area between fibers will determine spherulite size. As pointed out by Cogswell (1983), "Heterogeneities can act as nucleation sites and the fibers in composites are clearly heterogeneities with respect to the resin phase." Cogswell reports that, when cooling APC-1 rapidly from 380°C in the melt to a temperature in the range 20 to 200°C, the morphology is not significantly dependent on the processing history. In this particular sample a 35 percent crystallinity was measured by differential scanning calorimetry. Microscopy on the sample indicated that the spherulite size (the largest texture present) was about 2 μm . In a Boeing program sponsored by the Air Force a process optimization study was completed on APC-2 (Boeing Company, 1983). Various processing cycles were selected, effects on crystallinity and spherulite size were measured, and finally mechanical properties were measured. Table 5-1 shows the cycles studied and the expected results. The thermal cycles were performed in an autoclave, as shown in Figure 5-2. In addition "as-received" panels from ICI were also investigated. Examination of "as-received" laminates by plane polarized light micrographs of thin sections (3 μm) show a "typical" spherulite size of 15 μm . This "typical" spherulite size seems to be based on a measurement in a "typical resin-rich area" and not between a tightly packed fiber bundle encountered in a composite having a 60 percent fiber volume. The Boeing study indicates that the quenched and nonoptimum crystal growth conditions have similar features; spherulites were shown to be larger than in the "as-received" condition. It was noted that the time above melt and cooldown conditions selected for the process optimization study were designed to promote both fast and slow growth from a large or small number of nucleation sites rather than the rate of growth. In looking at the thermal cycle designed to promote optimum crystal growth rates from a large number of nucleation sites, the short residence time above the melt temperature did not allow complete melting, leaving a large number of nuclei available for initiation of crystal growth on cooldown. The spherulite structure was very

TABLE 5-1 Process Optimization Study

Process Cycle	Effect on PEEK Morphology	Effect on Composite Mechanical Performance
Quench	Low percent crystallinity	Tough, but lower matrix modulus equals reduced compression strength
Slow cool to nonoptimum crystallization temperature	Large spherulites	Decreased toughness
Fast cool to optimum crystallization temperature	Small spherulites	Increased fracture toughness

TABLE 5-2 Thermal Cycles for Process Optimization Study

Process Cycle	Conditions
Quench	Heat to 392°C (740°F), hold for 30 minutes then cool as rapidly as possible
Slow cool from above melt to nonoptimum crystallization	Heat to 392°C (740°F), hold for 30 minutes then cool to 320°C (608°F) and hold for 30 minutes; cool to room temperature
Fast cool to optimum crystallization temperature	Heat to 371°C (700°F), then cool to 230°C (445°F) and hold for 30 minutes; cool to room temperature

Note: ICI press molding cycle: 30 sec/ply, plus 5 min at 380°C (716°F). Transfer to 200°C (392°F) for 5 min; cooling rate, 40°C (72°F)/min.

small in this case, much smaller in fact than the "as-received" case. The conclusion is that crystal growth rates are apparently very rapid, growth must initiate soon after cooling below melt, and the spherulite size is very dependent on the number of growing spherulites.

Mechanical Properties Versus Morphology

A study was conducted in the Boeing program to evaluate the effects of changing the percentage of matrix crystallinity and matrix spherulite size on matrix stiffness and toughness-dominated composite performance.

Open-hole tension, open-hole compression, and compression-after-impact performance were chosen, they are all dependent on the matrix modulus and toughness. Data on these tests are shown in Tables 5-3 and 5-4 and in Figure 5-2. No significant statistical differences are evident; however, the quench condition strengths appear to be slightly higher than other cases for the open hole tension data. It was speculated that this may be caused by a lower crystallinity and thus greater matrix ductility, thereby reducing the stress concentration at the hole.

Open-hole compression tests results are given in Table 5-4. No differences in strength are evident at either room temperature or at 82°C (180°F) after moisture-conditioning. The quenched sample performed as well as the others, although it may be somewhat less crystalline. However, the tests are really not comparable, since the compression test was done after extensive hot, wet annealing.

Figure 5-2 shows the compression-after-impact results as a function of the processing conditions. The lower performance of the slow-cooled material (nonoptimum crystallinity) was attributed to large spherulites and a higher percentage of crystallinity. Conversely, the good properties after quenching could be due to the increased matrix toughness and ultimate elongation due to lower crystallinity.

TABLE 5-3 Summary of APC-2 Process Optimization Laminates Open-Hole Tensile Strengths

Condition	Failure Strength, MPa (ksi) at	
	54°C (130°F)	24°C (75°F)
As-received	411 (59.5)	401 (58.1)
Fast-cool	412 (59.8)	372 (54.0)
Slow-cool	411 (59.6)	381 (55.3)
Quench	427 (61.9)	403 (58.4)

TABLE 5-4 Summary of APC-2 Process Optimization Laminates Open-Hole Compression Strengths

Condition	Failure Strength MPa (ksi) at	
	24°C (75°F)	82°C (180°F)
As-received	295 (42.8)	268 (38.9)
Fast-cool	294 (42.7)	271 (39.3)
Slow-cool	292 (42.4)	265 (38.4)
Quench	290 (42.0)	268 (38.9)

Table 5-5 gives the percent crystallinity of the APC-2 heat-treated laminates as a function of various cooldown conditions. As expected, the crystallinity increases as the rate of cooldown decreases. Figure 5-3 illustrates the effect of crystallinity on compression-after-impact, and hot, wet open-hole compression strength. It was noted that a slight increase in

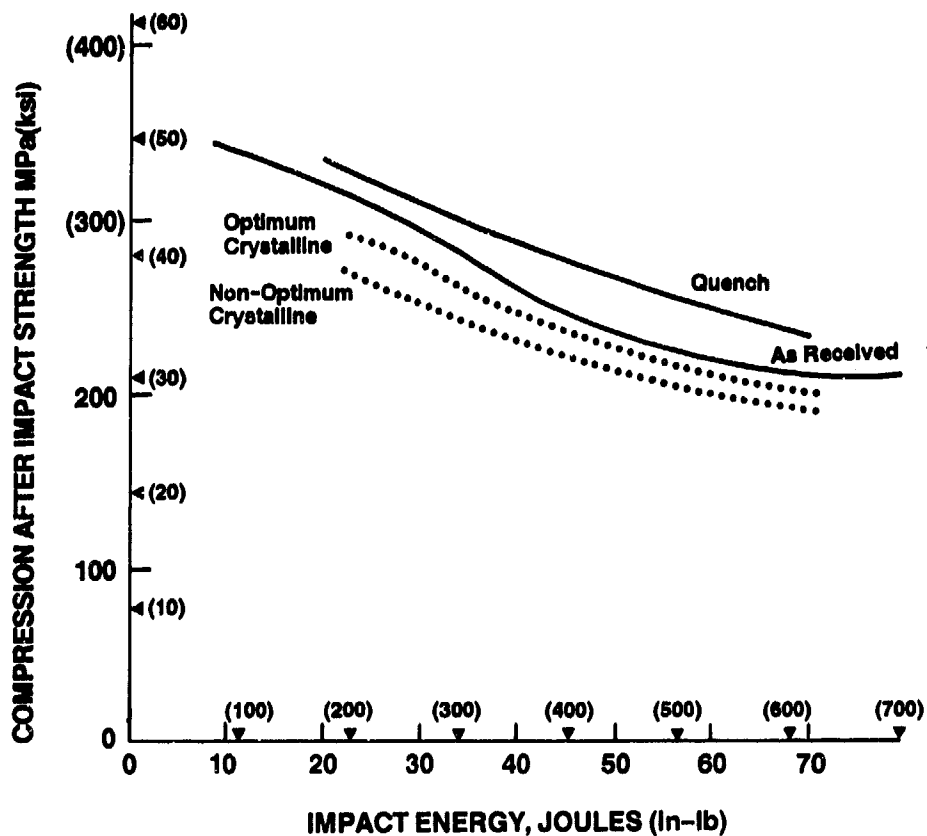


FIGURE 5-2 APC-2 compression-after-impact performance for process optimization laminates.

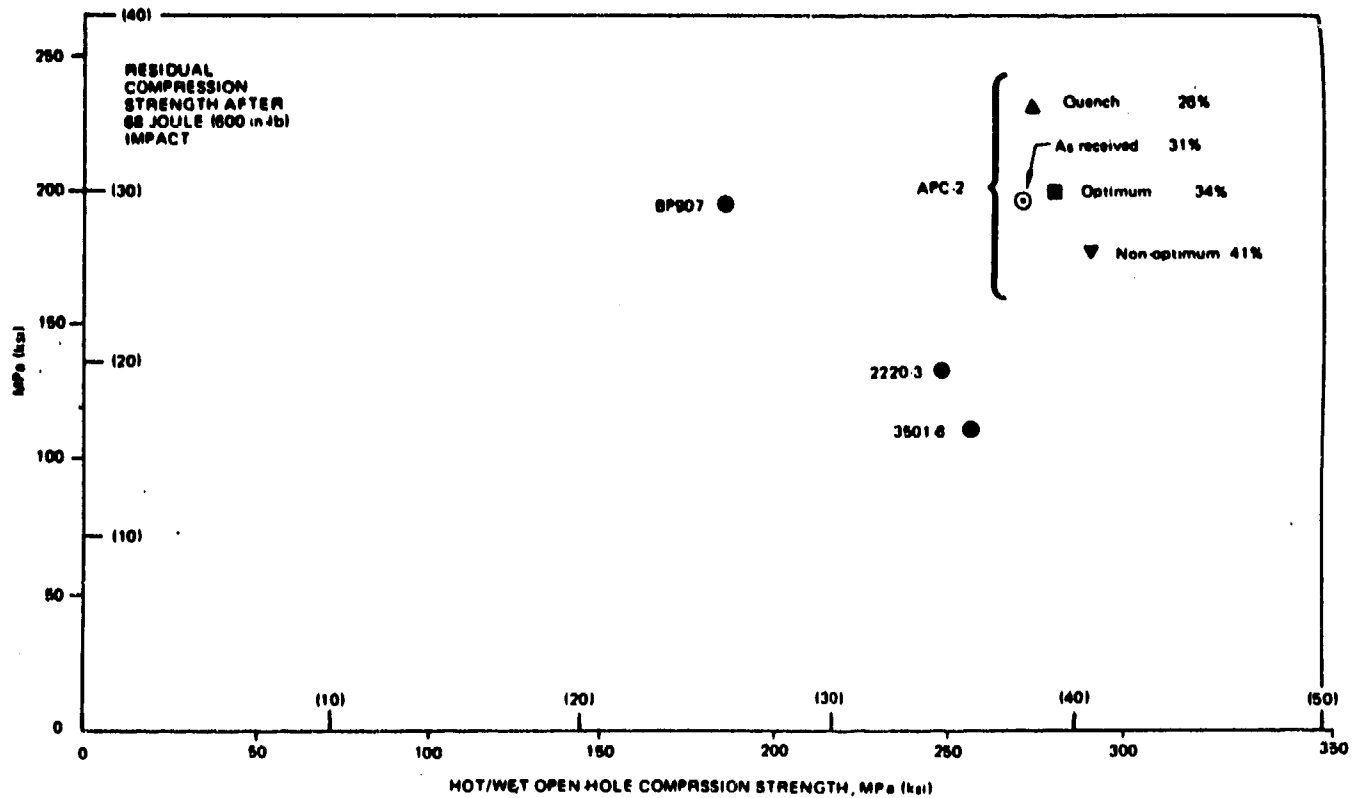


FIGURE 5-3 Residual compression-after-impact strength versus hot, wet open-hole compression strength for APC-2 process optimization laminates. Percent crystallinity is indicated.

TABLE 5-5 Percent Crystallinity for Heat-Treated APC-2 Laminates

Heat Treatment	Percent Crystallinity	Percent Crystallinity Calculated with 0.59 Fiber Fraction
As-received	30.8	
Optimum	32.7	34.1
Nonoptimum	37.8	41.3
Quench	23.1	26.3
1°/min	45.0	
Air Cool	33.0	
Water quench (1886°F/min)	29.0	

hot, wet open-hole compressive strength could be due to the increased matrix modulus from the higher crystallinity. The marked change in compression-after-impact strength is because the increase in crystallinity reduced the matrix ductility and toughness.

The report's concluding remarks note that the degree of crystallinity affected both stiffness-controlled tests (hot, wet open-hole compressive strength) and toughness-controlled tests (compression-after-impact strength). The effect of spherulite size was negligible; however, it may have a strong influence on crack growth rate in tests such as compression-compression fatigue of a compression-after-impact coupon.

Few morphology-property studies have been completed on the other grades of PEEK. These products are often produced from higher viscosity resins that have mobility in their molten state, which inhibits the formation of the type of spherulite structure encountered with the APC-2 material. What effects this may have on property relationships is unknown at this time.

Polyphenylene Sulfide

Studies have been completed at Phillips Petroleum Company by Beever and Ryan (1985) that evaluate the effect of processing on mechanical properties of polyphenylene sulfide-carbon composites. Composites were fabricated using prepreg containing polyphenylene sulfide (PPS) resin with Hercules' unsized AS-4 carbon fiber. The prepreg was heated to 316°C (600°F) at contact pressure in a preheated press for 4 minutes followed by 0.7 to 1.0 MPa (100 to 150 psi) pressure for an additional 3 minutes. The hot laminate was then transferred directly to a room-temperature press and cooled under 0.7 to 1.0 MPa (100 to 150 psi) pressure to 38°C (100°F). This usually took about 1 minute. The molded plaques were then tested in unannealed (amorphous, as-molded) and annealed (crystalline) forms. Annealing was accomplished by subjecting the laminates to a temperature of 200°C (392°F) for a period of 2 hours. Mechanical properties were then measured on plaques with crystalline and amorphous matrix. Similar processing conditions were used on 20-mil PPS sheet. Table 5-6 shows the effects of molding conditions on the properties of the neat resin. The effect of this processing on composite properties is shown in Table 5-7. No other processing conditions were addressed, such as slow cooling from the melt or maintaining temperature at an optimum crystallization temperature. Spherulite size was not measured, nor was any x-ray analysis done. Thermal analysis was run on the composite using differential scanning calorimetry. There was much speculation on the relationship between morphology and properties. Some or all of the speculation may be accurate, but there are no data to confirm the composite morphology, which may be considerably different from that of the neat resin. Annealing was assumed to produce small crystallites that improved composite properties. It was noted that annealing after quenching resulted in a fully crystallized matrix (35 percent crystallinity).

The amorphous composite matrix (quenched and unannealed) is tougher than the crystallized matrix composite, as evidenced by the higher transverse and G_{IC} values. In general, the differences are not very large except for compression properties. The softer amorphous matrix allows the fibers to buckle under compression, thus giving low compressive-strength values. After

TABLE 5-6 Effect of Thermal History on Mechanical Properties of Unoriented PPS Film

Property	Quick-Quenched, Unannealed	Quick-Quenched, Annealed at 200°C	Slow-Cooled, Unannealed
Density, gm/cc	1.3094	1.3458	1.3514
Percent crystallinity*	0	30.2	34.8
Tensile modulus, MPa	1926	2574	2709
Tensile break, MPa	44.5	80.7	51.3
Elongation at break, %	20.0	4.8	3.4
Tensile yield, MPa	63.6	-	-
Elongation at yield, %	5.0	-	-

*From density measurements: $\rho_a = 1.314$ gms/cc, $\rho_c = 1.43$ gms/cc

TABLE 5-7 Effect of Annealing on Mechanical Properties of Ryton PPS/Carbon Fiber^a Unidirectional Laminates

Property	Morphology	
	Unannealed	Annealed
Longitudinal tensile modulus, GPa (Msi)	131.0 (19.0)	135.0 (19.6)
Longitudinal tensile strength, MPa (Ksi)	1490.0 (216.0)	1641.0 (238.0)
Transverse tensile modulus, GPa (Msi)	9.0 (1.3)	9.0 (1.3)
Transverse tensile strength, MPa (Ksi)	36.6 (5.3)	31.7 (4.6)
Longitudinal flexural modulus, GPa (Msi)	118.0 (17.1)	121.0 (17.6)
Longitudinal flexural strength, MPa (Ksi)	1083.0 (157.0)	1290.0 (187.0)
Transverse flexural modulus, GPa (Msi)	7.6 (1.1)	9.0 (1.3)
Transverse flexural strength, MPa (Ksi)	56.6 (8.2)	53.1 (7.7)
Longitudinal compressive strength, MPa (Ksi)	338.0 (49.0)	559.0 (81.0)
Transverse compressive strength, MPa (Ksi)	103.0 (15.0)	124.0 (18.0)
Short beam shear strength MPa (Ksi)	69.0 (10.0)	---
G_{Ic} KJ/m ² (in.-lb/in. ²)	0.8 (4.4)	0.6 (3.4) ^b

^aPrepreg contains 68 ±2 wt% carbon fiber.

^bValues as high as 1.3 kJ/m² (7.8 in.-lb/in.²) have been obtained by film stacking.

annealing, the matrix is much stiffer and the compressive strength is almost twice as high.

Certain issues remain to be resolved:

- Changes in polymer morphology may occur as a function of composite processing.
- Polymer morphology, such as crystallinity, may vary through the thickness of a tapered or thick part.
- Variations in crystallinity in a part may result in changes in mechanical properties.
- Changes in polymer morphology may occur as a function of time and temperature.

FORMABILITY

Brewster and Cattanach (1983) found that the formability of a material depended on the forming temperature of the process and the drapability of the fiber orientation or fabric weave of the lay-up used. The author introduced a term called "pseudo-ductility," a characteristic that describes a material's ability to have relative movement within and between each ply. It was concluded that a material that demonstrated pseudo-ductility should be readily formable.

Within the ply, pseudo-ductility is required for forming compound contours and may be improved by the use of three separate mechanisms that are fundamental to textile technology. These mechanisms are (1) a "trellis effect" with the fibers hinging about their points of contact; (2) a "shear-slip effect" with the fibers sliding relative to each other; and (3) a "fiber flattening or straightening effect." These mechanisms are illustrated in Figure 5-4.

Between the plies, the pseudo-ductility mechanism is interlaminar slip, a feature that is necessary in countering fiber buckling. This mechanism can be easily recognized in the simple bend configurations shown in Figure 5-5.

In typical situations, sheets may be wholly or partly heated to a temperature at which the matrix will flow and permit these mechanisms to operate while forming a part.

Joining and Fastening

Thermoplastic composites, both long- and short-fiber reinforced, offer a broad spectrum of joining and fastening opportunities. Unlike their thermoset counterparts, the thermoplastic nature of the base matrix resins allows them to be melted after the part has been fabricated. This allows

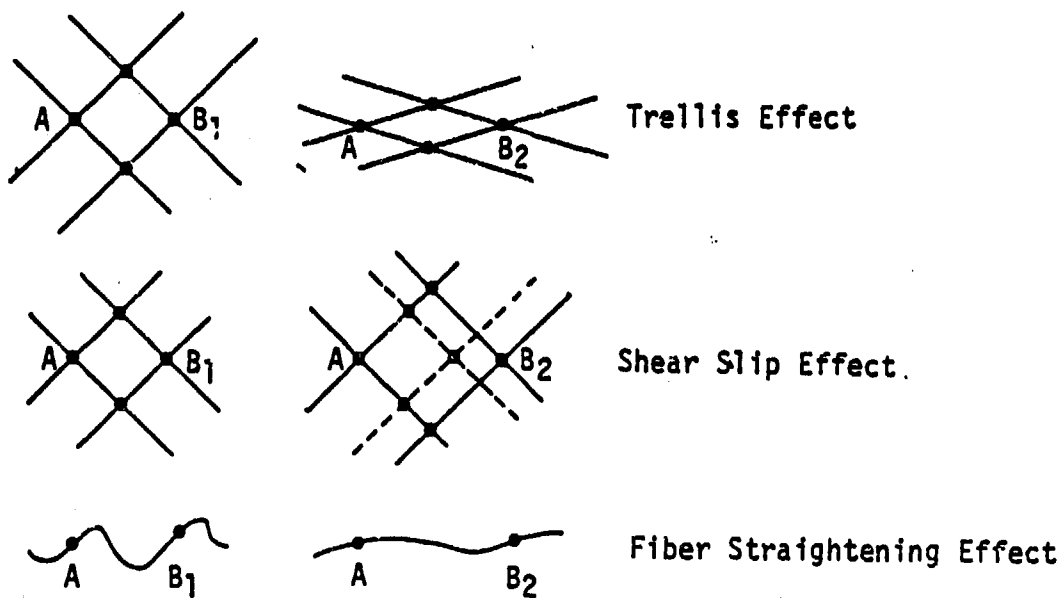


FIGURE 5-4 Pseudo-ductility of weaves.

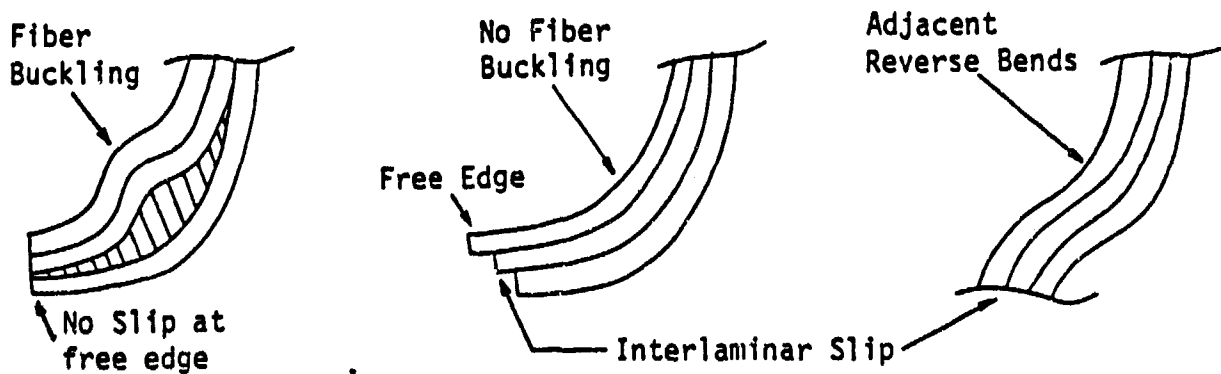


FIGURE 5-5 Interlaminar slip.

consideration of many new bonding techniques in addition to the use of adhesive bonding and mechanical fasteners.

These new techniques include electromagnetic bonding, friction joining, radio-frequency sealing, thermal bonding, and ultrasonic welding. Although these procedures vary in method, they all involve in essence a melt-bonding process. In each technique, energy is supplied to the thermoplastic composite materials being joined. The energy causes localized melting of the thermoplastic resin matrix, and bonding occurs at the interface between the two parts. Since the energy force can be focused and in most cases the response level of the resin matrix can be controlled, the melting and joining is localized and easily controlled. Excellent welds can be achieved with most thermoplastic composites, and these techniques offer the potential for quick, easy, economical, and reproducible bonding of thermoplastic composites.

Adhesive bonding is, however, still the most widely used method for plastics assembly, and thermoplastic composites can easily be adhesively bonded to a variety of substrates. As is the case in bonding other systems, proper surface preparation and care in selection of the adhesive system are extremely important. Epoxy, cyanoacrylate, and reactive acrylates are most often recommended for short-fiber-reinforced thermoplastic composite systems.

Integrating component parts and subassemblies into a complete structure often requires mechanical fasteners, particularly if maintenance or service to these structures is routine. Such fasteners can also double as spacers, insulators, thread covers, and protectors. These mechanical fasteners may be introduced during the molding cycle or in a post-molding operation and may be used with thermoplastic composites to join plastic-to-plastic, plastic-to-metal, plastic-to-wood, etc. Regardless of the application, it is always best to match the design of the fastener with the thermoplastic composite being used in the particular application.

In certain applications where repeated disassembly is not a routine occurrence, thermoplastic composites may be threaded directly to accept metal screws. Excellent pull-out strengths have been reported. Self-tapping screws have also been used with good results.

Quality Assurance

Compounding of high-performance thermoplastics with reinforcing fibers can be accomplished with a relatively high level of quality assurance. Fiber levels can be closely controlled, and reputable manufacturers of matrix resins and reinforcing fibers, in general, provide consistent and high-quality materials. Test specimens molded under controlled conditions provide consistent properties, and laboratory evaluation of test specimens serves as the basis for good materials quality control. Laboratory and molding viscosity and flow tests likewise serve as excellent quality-control tests relating to processibility.

Quality assurance of the final finished part or structure is, of course, a crucial concern. In general, the issues here are the same as for thermoset

composites. Resin, fiber, and void content are all important factors. Void content could be determined by techniques such as C-scan, acoustic emission, image analysis, and thermography as used for thermoset-based materials. For semicrystalline materials such as PEEK, which are dependent on crystallinity for development of desired properties, monitoring of this parameter is obviously required. The intensity of melt endotherms as measured by differential scanning calorimetry offers a practical approach to determining crystallinity.

At present there are two major quality assurance concerns that require additional attention in final part production. These are fiber-matrix interface and part and mold design. The fiber-matrix interface is an extremely important issue and is being examined by composite producers as well as fiber manufacturers. Poor interfacial interaction between the reinforcing fiber and the resin matrix generally manifests itself in substantial loss of composite property under high-temperature, high-humidity environments. Wicking of moisture into the composite along the fiber surface causes loss of adhesion of the resin matrix to the fiber surface and a subsequent loss of properties. Development of specific tailored silane coupling agents has solved this problem in many glass-reinforced systems, and good progress is being made in carbon-fiber and aramid reinforced systems.

The major quality and performance issue facing the short-fiber composites industry is part and mold design. Too often, ultimate composite properties are not translated into the final part because of improper mold design and/or molding procedures. All part and mold design and molding operations must take into account fiber breakage, fiber orientation, flow patterns, weld lines, etc. Improper mold design can result in failure at stress levels as low as 25 percent of ultimate.

With proper attention at all phases of handling, from raw materials production to final part production, high-quality parts can be produced. If thermoplastic composites are to be considered for high-performance parts, this issue is critical to success.

On-Line Process Control

The past 5 years have seen continuous fiber-reinforced laminates move from relatively thin flat laminates used mostly for secondary structures to thick (2 to 3 in.) laminates used for primary structures. Until recently, these laminates were almost exclusively made with thermosetting resins using a vacuum bag, autoclave process. In the production of thick laminate materials, two nagging problems have arisen: the growth of stable voids and irregular compaction, which results in resin gradients and hence gradients in properties through the thickness.

In the case of thermosetting materials, the complex curing process involves simultaneous heat, mass, and energy transport along with chemical reaction in a multiphase system with time-dependent material properties and boundary conditions. Modeling this process from first principles is extremely difficult, but some very recent progress has been made. Submodels have been created for the reaction kinetics (Loos and Springer, 1983; Dusi et al., 1983), the viscosity (Springer, 1982; Dusi et al., 1983), void stability and growth (Kardos et al., 1983), and resin flow in the laminate (Gutowski,

1985; Loos and Springer, 1983; Williams et al., 1984). Incorporation of the submodels into an overall master cure model is now under way, primarily in the aircraft industry (Campbell et al., 1985).

In the case of void stability and growth, the water concentration in the prepreg as well as the temperature and pressure profiles in the autoclave are the key parameters involved in eliminating the void problem.

As yet there is no well-accepted description of how the resin flows in the laminates during compaction in an autoclave process. It is known that the autoclave pressure is not transferred hydrostatically to the resin and that, once flow begins, the resin pressure drops dramatically within the laminate, probably due to the network of fibers acting as a spring.

In the case of thermoplastic composites, the problems of void formation and resin flow will again be important. Some of the approaches used in looking at thermosetting systems will be useful, but it is also likely that new understanding will be needed. For example, when a crystallizable polymer is used as a matrix, what will be the effect of the fibers on the crystallization kinetics?

In short, the thermoplastic composites possess many of the same processing problems inherent in thermosetting composites. Instead of reaction kinetics, the crystalline thermoplastic systems will require a crystallization kinetics model.

New sensor devices will be needed to probe the materials in real time and to feed back information on processing parameters, which in turn can be used for on-line control of the process.

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APPENDIX A

MOLDING TECHNIQUES

A wealth of literature exists related to nonreinforced and short-fiber-reinforced thermoplastic manufacturing processes, whereas only a few sources address manufacturing processes for continuous-fiber thermoplastics. The following manufacturing processes have all been used to either consolidate or form continuous-fiber thermoplastic details:

- Autoclave lamination and molding
- Continuous lamination
- Filament winding
- Pressure forming
- Pultrusion
- Roll forming
- Vacuum forming

These manufacturing processes are described in the ensuing sections.

AUTOCLAVE LAMINATION AND MOLDING

Hoggatt and coworkers (1980) found that an advantage of autoclave consolidation over other processing techniques is its ability to laminate large areas at one time. The cycle time of a small autoclave (4 ft diameter by 8 ft long) was 4 hours. This included bagging and debagging and allowed for a heat rise of 10°F/min with a 30-min hold at temperature followed by a 12°F/min cooldown to room temperature.

Lamination of 32 ft² resulted in costs of 0.125 hr/ft² to 0.041 hr/ft² when three sheets were laminated simultaneously. This low-cost consolidation was accomplished without major tooling expense.

Hoggatt and coworkers (1980) also investigated post-forming using an autoclave. With this process, pressure is used to form the part. The cycle time in the autoclave was approximately 3 hours, which was less than that used for consolidation because the hold time is not required. Also, the forming temperature was reduced because parts are heated to slightly above the softening temperature. The autoclave post-forming cycle is significantly less in time than the cure cycle for epoxy parts and therefore has economic advantages for producing large composite parts.

Voss (1974) investigated the effect of processing pressure on the mechanical properties of graphite-reinforced polysulfone composites. Laminates were fabricated at 650°F and 2000 psi initially, and then at pressures comparable to those obtainable in existing autoclaves at 100, 200, and 500 psi. Results of flexural and short-beam shear tests showed that lower processing pressures do not adversely affect the composite's properties.

As pointed out by Griffiths and coworkers (1984), cycle times when using autoclaves are prohibitively long compared to other processing techniques, and this nullifies one of the primary advantages of thermoplastics.

CONTINUOUS LAMINATION

The continuous laminator is a machine developed by Yates (1972) to produce flat thermoplastic laminates (Figure A-1). The concept of this process is to heat the fabric and polymer in prepreg form up to melt temperature and laminate it with other heated plies between chilled pressure rollers while tension is held at the fabric delivery spools. A schematic of this process is shown in Figure A-2.

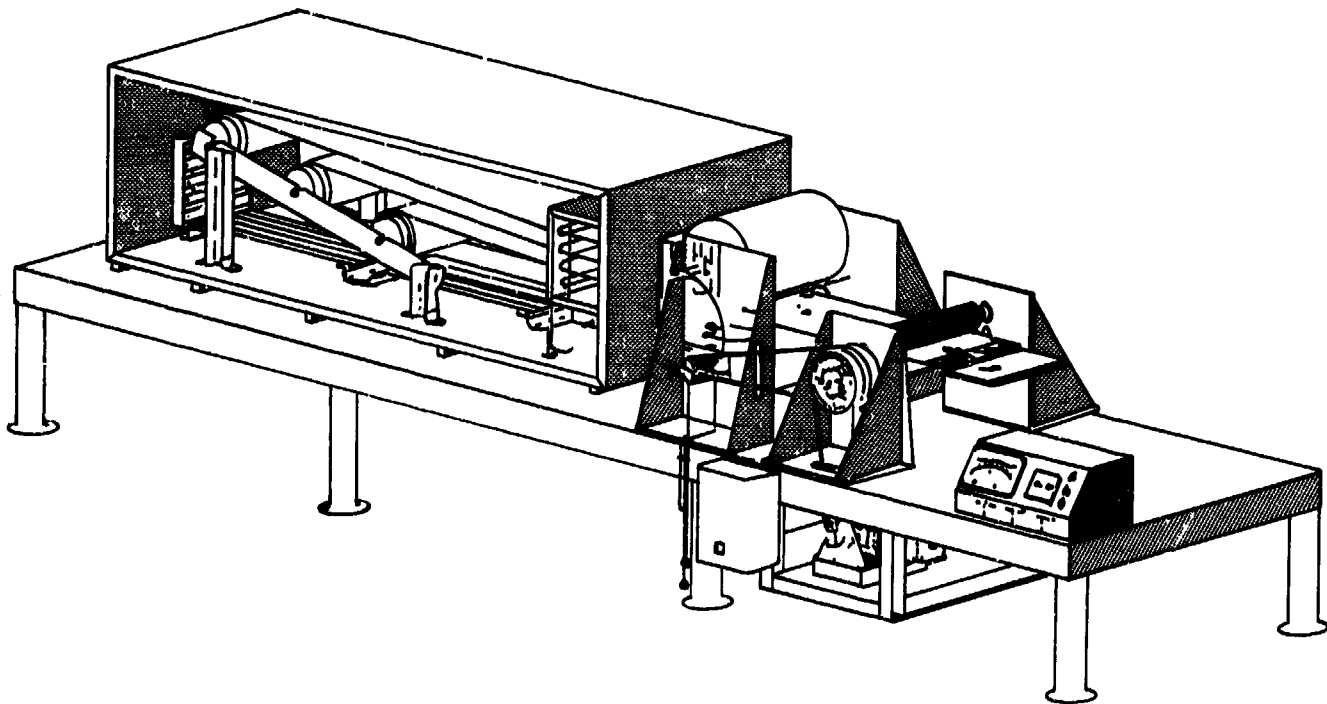


FIGURE A-1 Machine to produce continuous consolidated thermoplastic laminates.

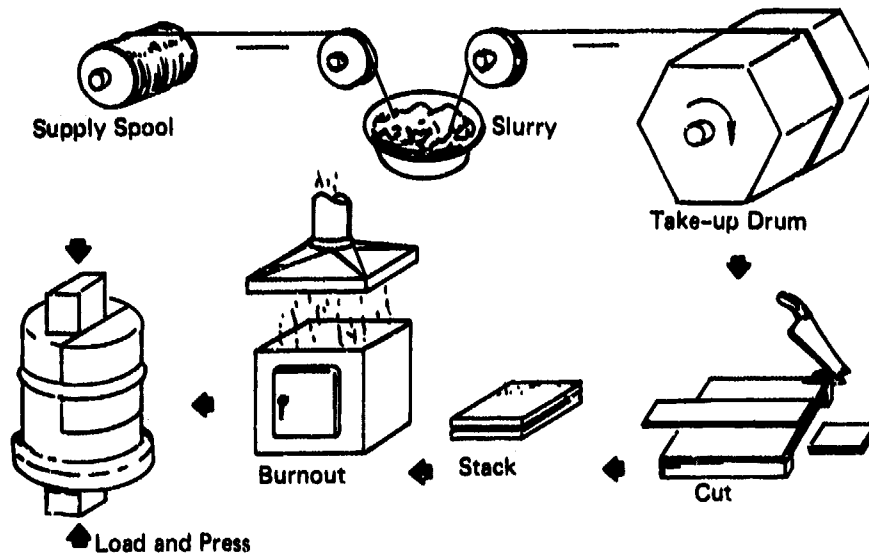


FIGURE A-2 Schematic of the process for glass matrix composite fabrication.

The temperature of the material was controlled primarily by the speed at which it passed through the heater. Laminating speeds of over 20 ft/min were achieved by Yates with three plies of 120-style fabric.

The basics that Yates learned from filament winding with thermoplastic prepreg were that the roving had to be heated to the thermoplastic's melting point just as it was delivered onto the mandrel and that the material already on the mandrel at the point of application needed to be at the same temperature in order to facilitate adequate compaction and fusion. Of the polymers evaluated, polycarbonate was the most adaptable to this process.

Other processors, including Goldsworthy Engineering and McClean Anderson, are developing similar filament winding techniques using thermoplastics.

PRESSURE FORMING

Pressure forming to date is the most successful technique used for manufacturing continuous-fiber thermoplastic components (Griffiths et al., 1984). To make a component, the thermoplastic prepreg is heated to a temperature of about 600 to 750°C and then pressed to final shape on cold tooling. The material has to be removed from the heat source and pressed within a very short period of time (12 seconds). Devices used to heat the prepreg for this process include infrared and high-mass ovens. The use of

matched metal tooling for press forming has proved to be unsuccessful. The very rapid cooling of the composite after contact with cold tooling does not allow the material to flow sufficiently throughout the laminate, resulting in areas of delamination and fabric distortion. Normally, a metallic alloy like aluminum is used for female tooling and silicone rubber for male tooling.

Press lamination studies were performed by Hoggatt et al. (1980), which resulted in a 2-hour cycle for a 4-ft² flat laminate (0.5 hr/ft²). The time per unit area was dependent on the capacity and capability of the press utilized. If the press had rapid heating or cooling capability, the cycle time could have been reduced. The 2-hour cycle was based on a part and mold assembly heat-up rate of 10°C/min from room temperature to 650°C and cooldown to 100°C. The cycle time could have been reduced to 1.25 hours if the part and mold were preheated to 350°C prior to insertion in the press, and then molded at 600°C and 200 psi and removed at 300°C on the cooldown cycle.

Consolidation costs could have been further reduced by laminating multiple sheets at one time using a separator ply between layers. Cycle time per unit area of laminate drops 80 percent when using the multisheet technique based on the molding of three sheets simultaneously.

Experiments with hydroforming have been shown by Brewster and Cattanch (1983) to be a promising candidate as a process for thermoforming aromatic polymer composite blanks. One reason hydroforming of thermoplastics is so attractive is that it takes advantage of sheet-metal forming technology that has been in development for many years. High pressures and low cycle times are inherent advantages of hydroforming.

The hydroforming process is based on the three tool configurations shown in Figure A-3. The tools can be described as (1) a male tool where the blank is formed around the outer surface of die; (2) a cavity tool where the blank is formed around the inner surface of the die; and (3) a double-acting tool, which requires a press that closes in two stages--the first to hold down the perimeter of the blank and the second to engage a punch to form the blank.

FILAMENT WINDING

The process of filament winding thermoplastics has been shown to be a viable alternative to other processes. Prewo and Minford (1985) used the filament winding process shown in Figure A-2 to fabricate a graphite fiber-reinforced glass-matrix laminate.

A typical processing cycle consists of the following steps:

- Impregnate graphite fiber tows with a slurry of finely divided glass powder particles and a binder.
- Collimate the impregnated fibers to form a tape and dry tape to form a prepreg.
- Cut and stack tape plies in a shaped die.
- Heat to remove binder.

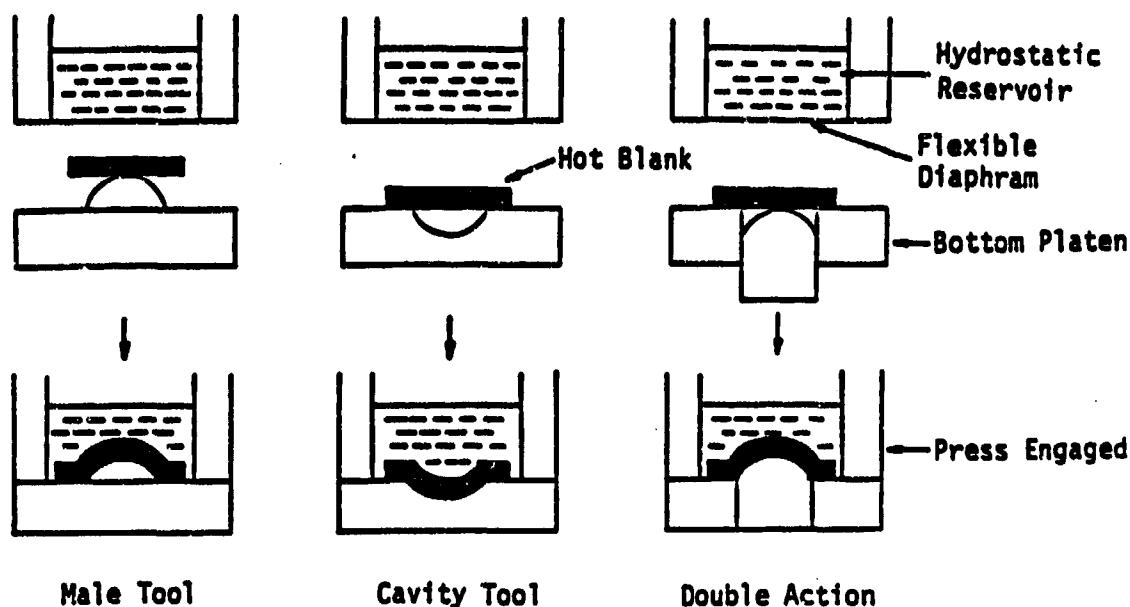


FIGURE A-3 Hydroform principle and tool types.

- Heat die in an inert atmosphere and apply pressure to densify glass powder.
- Cool and remove fully dense part.

Four thermoplastic matrix systems were investigated by Yates (1972) for their processibility with filament winding and continuous laminate fabrication. The systems were polystyrene, polyphenylene oxide, polycarbonate, and polysulfone. Each of these systems was solution-impregnated into glass fibers using either methylene chloride or chloroform as a solvent.

PULTRUSION

Pultrusion using continuous-fiber thermoplastics has been successfully demonstrated by Goldsworthy Engineering. Under a contract with NASA, Goldsworthy Engineering developed a process to pultrude a carbon-polysulfone ribbon. Prepreg carbon tow is pulled from creels through a carding plate and drawn longitudinally onto a stationary mandrel, after which a ring-shaped winding head applies additional carbon fiber, laying it down in a 45-degree-pattern around the longitudinal tow "tube." Next, the wound prepreg tube is pulled through an induction heating station that melts the polysulfone. The molten tube is then squashed flat and consolidated into ribbon form by continuous opposed-belt laminating.

Existing graphite-epoxy pultrusion equipment was modified by Hoggatt et al. (1980) to provide higher temperature and pressure capabilities for use with thermoplastics. Three basic polysulfone-graphite pultruded shapes were fabricated. These were 3-in. wide solid laminates, 1-in. by 1-in. angles,

and a 0.040-in. by 3-in. wide sandwich. The best results with 11- and 18-ply laminates were obtained at temperatures of 600°C and pressures of 200 psi at pull speeds of 2 in./min. Angle sections with 12 plies yielded the best results under approximately the same process conditions. Sandwich panels were made using woven fabric face skins and polyimide core. Although the feasibility of producing sandwich sections was established, the finished parts had insufficient peel strength between the face skins and the core because of inadequate adhesive filleting. Inspection of sectioned parts showed them to be well compacted and free of voids.

ROLL FORMING

Promising results have been obtained by Brewster and Cattanch (1983) in roll-forming preheated thermoplastic blanks into straight and curved structural sections.

From experience thus far, the process of roll-forming a preheated thermoplastic strip would use cold metal roll-forming machines and techniques with conventional unheated steel rollers. Forming speeds of 50 ft/min have been attained, but it has been found that consolidation quality drops at higher speeds. Consolidation quality has also been found to suffer in areas on the parts that are not in direct contact with the rollers, most notably in angles of complex geometries.

The profile of the rolls is developed sequentially in what has been termed a "flower" pattern, as seen in Figure A-4, from the almost flat to full-form configurations. The preheated thermoplastic strip is pulled through the machine by virtue of increasing roll diameters at synchronous rotational speeds. Overstraining of the strip as it is being pulled through the rollers was found to be a concern and was accounted for by additions of 0-degree-ply in the lay-up, particularly on the external faces of the strip.

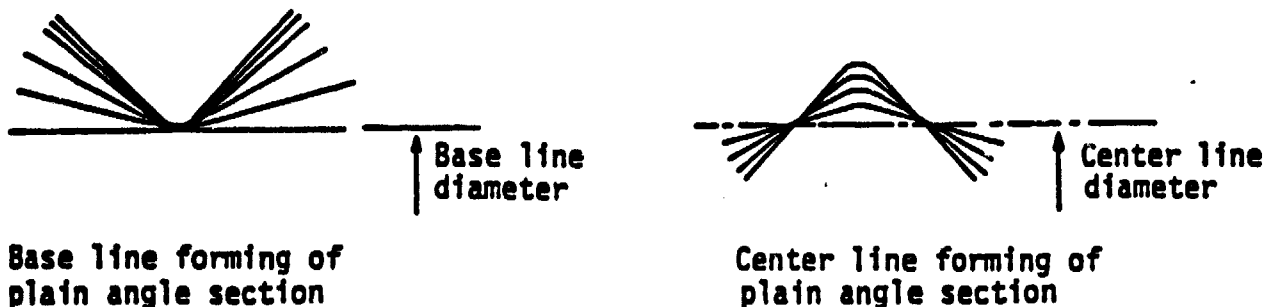


FIGURE A-4 Typical forming "flowers."

Early work on roll-forming has produced top-hat sections of uniform and locally reinforced stepped thicknesses, symmetrical and odd-legged section geometries with straight and curved lengths. The sections have been produced by combining angled sections between side rollers and forming a single consolidated part by applying heat and pressure.

VACUUM FORMING

Hoggatt and co-workers (1980) found that vacuum forming, shown in Figure A-5, proved to be a cost-effective method of making parts. First, the laminate is heated to 550 to 600°C and then formed over an aluminum tool with vacuum pressure. When full vacuum was on the part, the forming cavity was pressurized with plant air (80 psi) to consolidate the part. The laminate was then cooled and removed. Time studies on a production basis showed parts could be produced on a 10- to 20-min cycle. The dominant variables governing the cycle time were part thickness and heat transfer to the part. Vacuum forming was found to produce extremely accurate and reproducible parts. The process could be improved by increasing the auxiliary air pressure from 80 to 150 psi. This increased air pressure produces a high-quality structural laminate in all configurations.

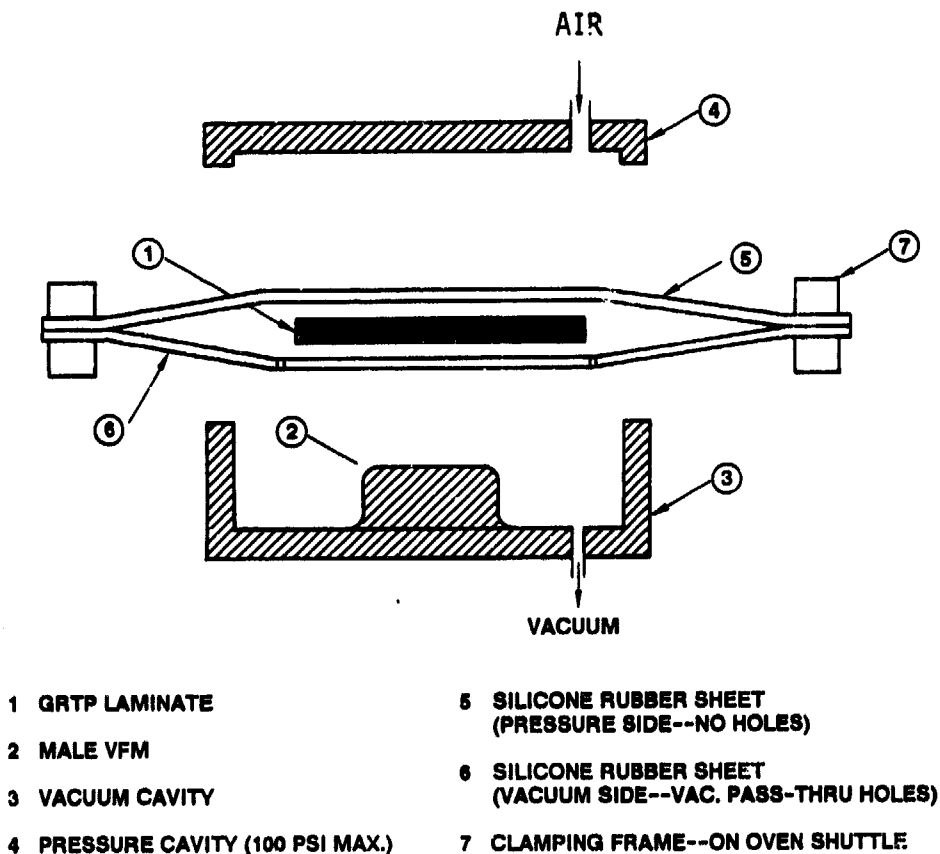


FIGURE A-5 Vacuum forming process for thermoplastic laminates.

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APPENDIX B

COMPONENT FABRICATION

Once the thermoplastic laminate has been consolidated using one of the manufacturing processes discussed earlier, additional thermoforming, or just the assembly of preformed details, may be needed to complete the finished product.

Poveromo and coworkers (1981) have developed a composite beam builder based on the automated aluminum beam builder built by Grumman under a NASA contract. The composite beam builder used a preconsolidated graphite/acrylic (forming temperature of 284°F) ribbon initially, and later was updated to use a preconsolidated graphite-polyethersulfone (forming temperature of 500°F) ribbon. Poveromo and co-workers claimed successful results in forming graphite-polyethersulfone beam cap sections, as seen in Figure B-1.

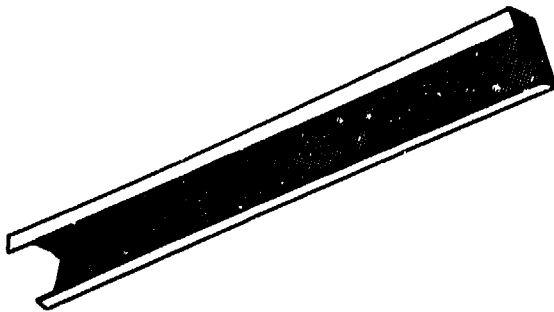


FIGURE B-1 Graphite-polyethersulfone beam cap specimen (Griffiths et. al., 1984).

Griffiths and coworkers (1984) of Westland Helicopters are involved in a program to produce a tail plane for a Westland 30 helicopter (Figure B-2)

made of aromatic polymer composite material. Griffiths reported one basic method was used to produce all ten components of the tail plane. The technique consists of laminating the material to the correct lay-up in the flat. After lay-up and tacking together, the sheet is hot-pressed. To obtain a well-consolidated sheet, pressures of 10 atmospheres with temperatures of about 752°F are utilized. For sheets of uniform thickness, the press faces can be used directly. For complex lay-ups, a flexible diaphragm must be used. To obtain good-quality sheets, the most direct solution is to use a large press, but for development work the use of "step-pressing" has been found adequate.

Tooling of various types has been tried in producing parts for the tail plane. Matched metal tooling was not successful. The very short period for which the composite stays warm, after contact with cold tooling, does not allow the material to flow sufficiently to produce even pressures throughout the laminate. The result is a component with areas of delamination and fiber distortion. This work has indicated the need to maintain a uniform pressure on the component from the moment it begins to be shaped until it is cooled to

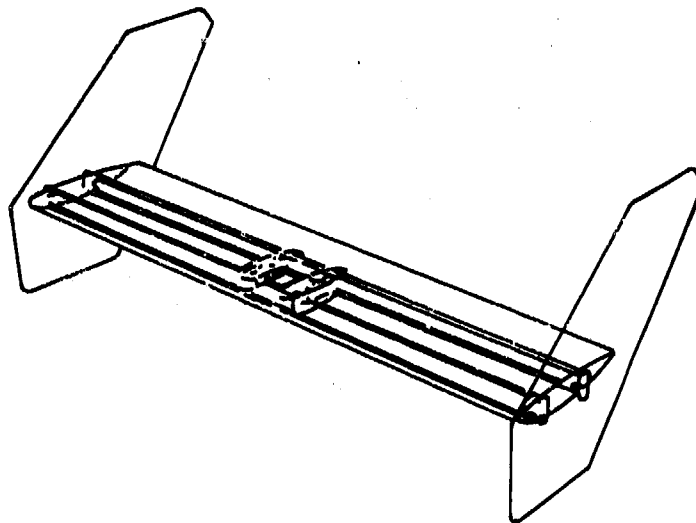


FIGURE B-2 Thermoplastic composite tail plane (3 ft by 9 ft) (Griffiths et al., 1984).

a temperature at which the matrix has solidified. Hydroforming has been found to achieve this goal quite well, but, because of limited machine size, components larger than 18 in. could not be made. Larger parts for the tail plane were press-formed with a rigid aluminum alloy female tool and silicone rubber male tool.

The components of the tail plane were then assembled in two stages. First, the skins were bonded to honeycomb core using an epoxy adhesive. The tail plane was then assembled on a mandrel and bonded in an oven under vacuum pressure.

Hoggatt and coworkers (1980) built a full-scale thermoplastic elevator torque box for a YC-14 aircraft, as shown in Figure B-3. For this component the P-1700 polysulfone resin was selected and used with A-S unidirectional graphite fibers (Hercules 3004/A-S/P1700 prepreg) and with T-300 woven graphite fibers (Hexcel T-3004/23x24, 811 Satin Prepreg).

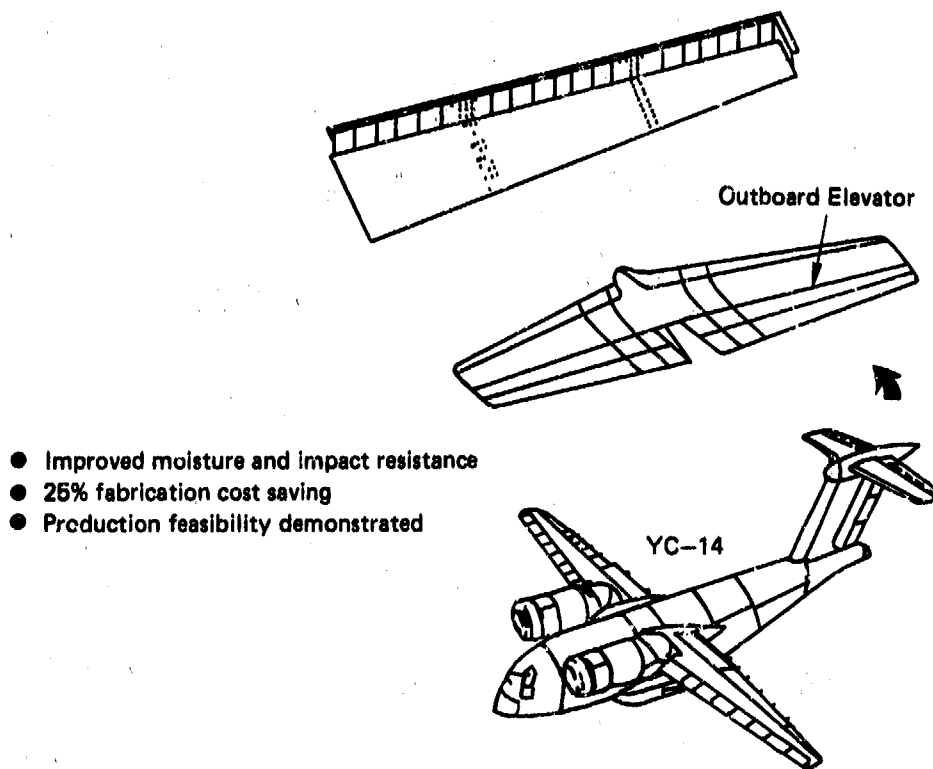


FIGURE B-3 Continuous graphite fiber-polysulfone elevator torque box for a YC-14 (Hoggatt et al., 1980).

Front and rear spar stiffeners were molded using match-die tooling. A four-ply premold material was placed in a die and then put in a press. This assembly was heated to 650°C and held at 200 psi for 15 min. The dies were then removed from the hot press and placed in a cold press until parts cooled below 250°C.

Rib details were also molded using match-die tooling. The male tool was machined from plate and the die cover was formed in a hydropress. The rib materials, four plies of fabric at 45°, were preformed in a press at 600°C and 200 psi. The precompact ribs were then bagged and heated in an autoclave to 600°C for 30 minutes at 200 psi to complete their fabrication.

The lower chords and skins were assembled by fusion bonding, and the balance of the elevator subassemblies were assembled by adhesive bonding. The adhesive used was Hysol 9628, which was cured in an autoclave at 250°C and 50 psi.

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APPENDIX C

SHORT-FIBER-REINFORCED THERMOPLASTICS

Short-fiber-reinforced polymers were developed largely to fill the property gap between continuous-fiber laminates used as primary structures by the aircraft and aerospace industry and unreinforced polymers used largely in non-load-bearing applications. In some respects the short-fiber systems couple advantages from each of these property-bounding engineering materials. If the fibers are sufficiently long, stiffness levels approaching those for continuous-fiber systems at the same fiber loading can be achieved, while the ability of the unreinforced polymer to be molded into complex shapes is at least partially retained in the short-fiber systems. Thus, short-fiber-reinforced polymers have found their way into lightly loaded secondary structures, in which stiffness dominates the design but in which there must be a notable increase in strength over the unreinforced polymer. An additional advantage of short-fiber systems is that the use temperature at which room-temperature properties can be maintained is significantly increased over that for unreinforced or even particulate-reinforced systems. Short-fiber-reinforced crystalline thermoplastics are particularly noteworthy, there being an increase in the heat distortion temperature under load (HDUL) of as much as 80°C over the unreinforced system when a 20 wt percent fiber loading is used. Designers are now utilizing the processibility of short-fiber molding compounds along with continuous-fiber prepreg to develop hybrid structures consisting of short-fiber core material enclosed by continuous-fiber skins.

Despite these advantages, short-fiber-reinforced thermoplastics have their own set of problems, to which we will allude in the following sections. For a discussion of the matrix polymers used for short-fiber systems of interest to this study, the reader is referred to Chapter 4.

SHORT FIBERS FOR REINFORCEMENT

Fibers used in reinforcing thermoplastic composites include glass (E and S), carbon, aramid, and a variety of "whisker" materials, some of

which can now be produced in continuous form. Typical properties of these fibers are given in Table C-1. Other reinforcement and filler materials are available in various forms (e.g., bead, sphere, platelet, particulate) but are not generally considered as major reinforcing components in engineering applications requiring high strengths. Glass fiber is the most widely used form of fiber reinforcement in short-fiber-thermoplastic composites. Fiber prices range from about 70 cents to \$3.50 per pound.

TABLE C-1 Nominal Properties of Reinforcing Fibers

Fiber Type	Fiber Form	Density g/cc	Tensile Strength, 10 ⁵ psi	Young's Modulus, 10 ⁶ psi
E Glass	Roving, chopped strand	2.6	5	11
S Glass	Roving, chopped strand	2.5	7	12
High-modulus carbon	Roving, chopped strand	2.0	3	60
High-strength carbon	Roving, chopped strand	1.7	4	40
Silicon nitride	Whisker	3.2	20	57
Silicon carbide	Whisker	3.2	15 to 20	70
Silicon carbide	Chopped fiber	3.2	3.5	24
Aramid	Roving, chopped strand	1.5	5	18
Alumina	Chopped yarn	4.0	2.1	28
Steel	Chopped filament	7.87	4 to 6	29

Carbon fiber is rapidly establishing itself as a top candidate for high-performance applications. It is available in forms that offer high strength, high modulus, dimensional stability, electrical conductivity, inherent lubricity, excellent corrosion resistance, heat resistance, and low density. Prices have declined from over \$200 per pound in 1969 to \$17 to \$35 per pound in 1985. Pitch-based fibers using new technology are expected to be available at \$5 per pound within 2 to 4 years.

Aramid (Kevlar) fiber is a synthetic organic fiber. It was introduced commercially in 1972 primarily to replace steel fiber in radial tires. Because of its high strength, light weight, and inherent toughness, it is finding increasing use as a reinforcing fiber in industrial, military, and aerospace composite applications. Aramid fiber prices range from \$10 to \$30 per pound.

In addition to inherent fiber properties and fiber lengths, the fiber-resin matrix interface also plays a major part in composite strength and performance. Accordingly, the fiber surface in most composite systems must be treated to maximize resin-fiber interaction. Most experts agree that good adhesion between fiber surface and matrix resin is critical in maximizing properties and minimizing sensitivity to moisture. During their manufacturing, glass fibers are treated with a protective coating formulation to allow easy processing and to minimize fiber damage. This coating can be removed or additional ingredients can be added to arrive at a final package that maximizes fiber-resin adhesion. Organosilane compounds are the materials most often used to serve as coupling agents between glass fiber and thermoplastic resins. Each base resin matrix requires its own sizing package to achieve best performance.

Carbon fibers used in injection molding compounds generally also contain a surface coating to facilitate handling of fibers, particularly in the chopped strand form. Historically, these coatings have been optimized for and based on thermosetting resin systems. These systems are not often compatible with thermoplastics. In addition, carbon fibers often are given a special surface treatment (e.g., chemical or electrical oxidation) to alter surface energy characteristics. Excellent progress is being made in developing surface treatment and/or coupling additives for carbon fiber-thermoplastic composites. However, most systems have not yet been optimized.







Aramid fibers are also offered with a surface finish to improve handling and to improve interfacial interactions. As is the case with carbon fibers, most emphasis has been placed on improving interactions with thermosetting resin matrices. It is not surprising that these systems are not yet optimized for thermoplastic matrix resins.

Metal fibers, metallized glass, and metallized carbon fibers are also available. At present, these fibers have not achieved widespread use and are not considered a major factor in the fiber reinforcing arena. However, they are being successfully utilized in specialty applications where electrical conductivity, static charge dissipation and electromagnetic interference shielding are important considerations.

MECHANICAL PROPERTY PERFORMANCE AND LIMITATIONS IN SHORT-FIBER SYSTEMS

Table C-2 illustrates the wide range of mechanical properties imparted to composites by fiber geometry and orientation for a glass fiber-epoxy system. Both the modulus and strength data are bounded on the lower side by the particulate (sphere)-reinforced material while the upper bound in both cases is given by the continuous-fiber-reinforced systems. Between these two bounds lie the discontinuous-fiber-reinforced systems on which this appendix is focused. It is these systems, wherein fiber loading, aspect ratio, and orientation distribution all can vary, that present very challenging problems in property prediction and utilization.

TABLE C-2 Experimental Stress-Strain Data for a Variety of Glass/Epoxy Systems

System (Stress Direction)	Filler Shape and Orientation	Strength, $\times 10^{-3}$ psi	Stiffness, E $\times 10^{-6}$ psi	Ultimate Strain, ϵ , %	Volume Fraction Filler, V_f
Unfilled resin		10 to 12	0.3 to 0.4	4 to 5	0
Bead filled		9 to 10.5	1.5 to 1.7	2.0 to 2.5	0.50
Short fibers (transverse)		5.5	1.4	0.4 to 0.5	0.50
Short fibers (longitudinal)		40	4.5	0.6 to 1.0	0.50
Continuous fibers (transverse)		4 to 6	1.8 to 2.1	0.4	0.60
Continuous fibers (longitudinal)		130 to 160	6.3 to 6.8	2.0	0.60

In Table C-2 and subsequent illustrations, data are presented only for epoxy matrix systems because that data base is currently more accurate and complete. Exactly the same trends are found in short-fiber-reinforced thermoplastics.

ORIENTATION DISTRIBUTIONS

It is clear from the foregoing discussion that fiber orientation distribution is one of the most crucial of the variables that determine the mechanical properties of short-fiber composites. Yet the technical literature abounds with (1) data comparisons between samples that have been processed differently but assumed to have the same fiber orientation or (2) data compilations for systems for which the orientation distribution has not even been measured. One reason this occurs is that it is often difficult to measure the fiber orientation distribution. If the matrix is amorphous and the fibers crystalline, wide-angle pole figure X-ray analysis may be utilized to provide the distribution (Schierding, 1968). If the matrix is transparent, Fraunhofer diffraction may be used (McGee and McCullough, 1984), or a small fraction of the glass fibers may be prestained with an optically opaque dye and the distribution obtained from image analysis (Kardos et al., 1983). Three-dimensional orientations may be characterized by sectioning the sample along orthogonal planes and analyzing the fiber images on each of these planes (Goettler, 1970; Lovrich and Tucker, 1985; Fakirov and Fakirova, 1981). Quantitative descriptions of planar and axially symmetric orientation states have been developed by Pipes and coworkers (1982). New convenient methods need to be developed for characterizing the fiber orientation distribution of short-fiber composites.

GENERAL APPROACHES TO PROPERTY PREDICTION

The existing approaches to predicting the mechanical properties of short-fiber-reinforced polymers separate the analysis into two parts: (1) the specification of the properties of a representative volume element (RVE) and (2) the specification of a procedure by which the projections of the tensorial properties of the collection of RVEs can be volume-averaged subject to an orientation distribution.

The methods used in part 1 to predict the properties of the individual RVEs are reviewed by Kardos (1973) and McCullough (1977). In all these methods the RVE is viewed as a microscopic local region comprised of aligned fibers with a uniform but arbitrary aspect ratio. The general treatment by Wu and McCullough (1977) consolidates the various approaches through the notion of a reference elasticity. Specification of the reference elasticity generates upper and lower bounds as well as other models as special cases. In particular, the general model contains the popular Halpin-Tsai relationship as a special case in the limit of an infinite aspect ratio. Different results are obtained at aspect ratios less than 100. McCullough and coworkers (1983) proposed a model that treats the reference elasticity as that of a composite comprised of spherical beads of the same material as the short fiber and at the same volume fraction as the short fiber. This model incorporates certain correlations and gives improved results. The properties of the reference material are computed from a well-verified model for particulate composites (McGee and McCullough, 1981).

The format used in part 2 for obtaining the volume average of general second-rank tensors (e.g., coefficients of thermal expansion) and fourth-rank tensors (e.g., elastic constants and compliance constants representing the properties of the individual RVEs) is tedious but straightforward. The strategy for the reduction of these relationships to useful forms consists of isolating the invariants and reorganizing the relationship to emphasize rescaled orientation parameters related to the moments of the orientation distribution of the RVEs. The results for the orientation average of a general second-rank tensor B and a contracted fourth-rank tensor A subject to a two-dimensional planar orientation were reported by McCullough and coworkers (1983). McGee and McCullough (1984) developed a laser scattering device to experimentally characterize intermediate states of orientation.

The results for the orientation averaging of a general fourth-rank tensor (McCullough, 1977) subject to a three-dimensional axial orientation were reported by McCullough and coworkers (Wu and McCullough, 1977; McCullough et al., 1976). Again, the characteristics of this distribution are specified in terms of two orientation parameters. This type of orientation can result in a true three-dimensional random orientation as a special case; however, at intermediate states of orientation the results are limited to transverse isotropy around the unique axis.

McGee (1982) reported the results for second- and fourth-rank tensors averaged under a more general three-dimensional orientation distribution. This formulation contains four orientation parameters. Both the two-dimensional planar and three-dimensional axial orientation distributions are contained as special cases.

The subtle issue involved in applying these relationships is the specification of the tensorial quantities that are the object of the averaging process. The popular "laminate analogy" (Halpin, 1984; Halpin and Kardos, 1978; Tsarnas and Kardos, 1985) illustrated in Figure C-1 arbitrarily selects the elastic constant array as the averaging object. This selection, as implied by the construction of Figure C-1, assumes a uniform strain throughout the system. Christensen (1979) justifies this assumption by restricting attention to random fiber systems in which the aspect ratio approaches infinity. Alternately, the compliance constant array could be selected as the averaging object. This selection suggests the "side-by-side" aggregation illustrated in Figure C-2 rather than stacked laminar and implies a condition approaching uniform stress throughout the system. The results from these two selections of averaging objects differ significantly.

Comparisons with experimental data (Halpin, 1984; McCullough et al., 1983) suggest that the selection of the elastic constant array as the averaging object may be adequate for sheet molding materials. This is rationalized by the argument (McCullough et al., 1983) that the RVEs are strongly connected by common filaments so that a condition approaching uniform strain may exist. McCullough (1983) cautions that systems comprised of much shorter filaments could mitigate this condition so that the behavior could tend toward averages conducted on the compliance array.

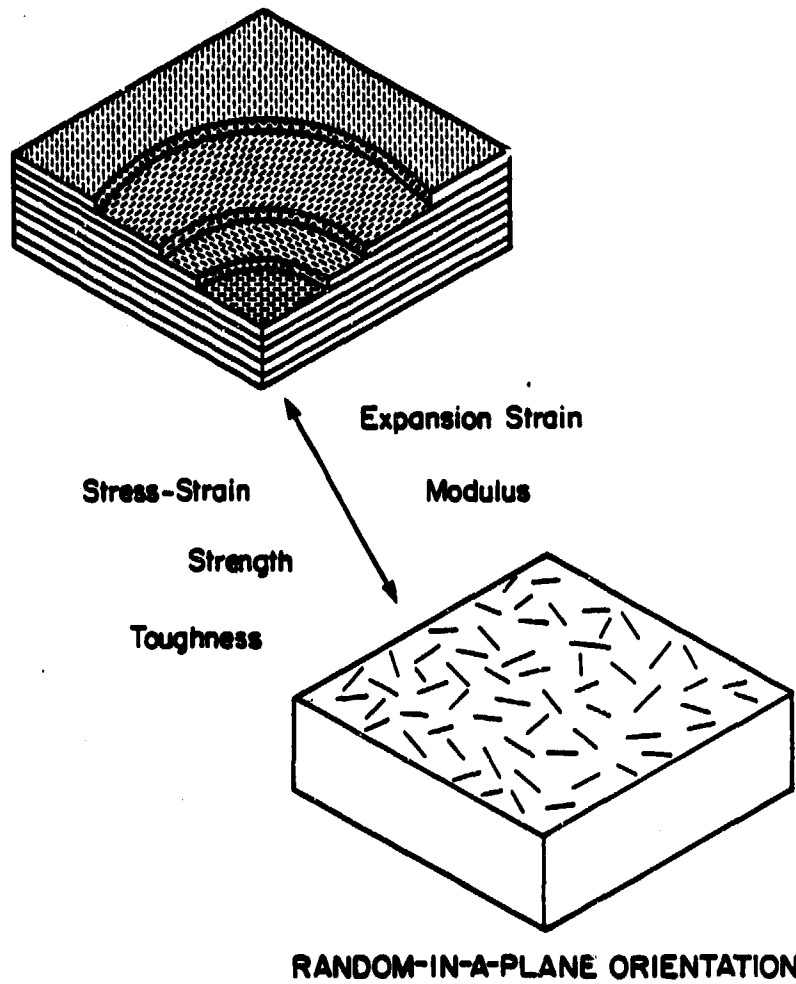
QUASI-ISOTROPIC LAMINATE

FIGURE C-1 Schematic design of laminate analogy for predicting mechanical properties of two-dimensional short-fiber composites (Kardos, 1973).

AGGREGATE MODEL

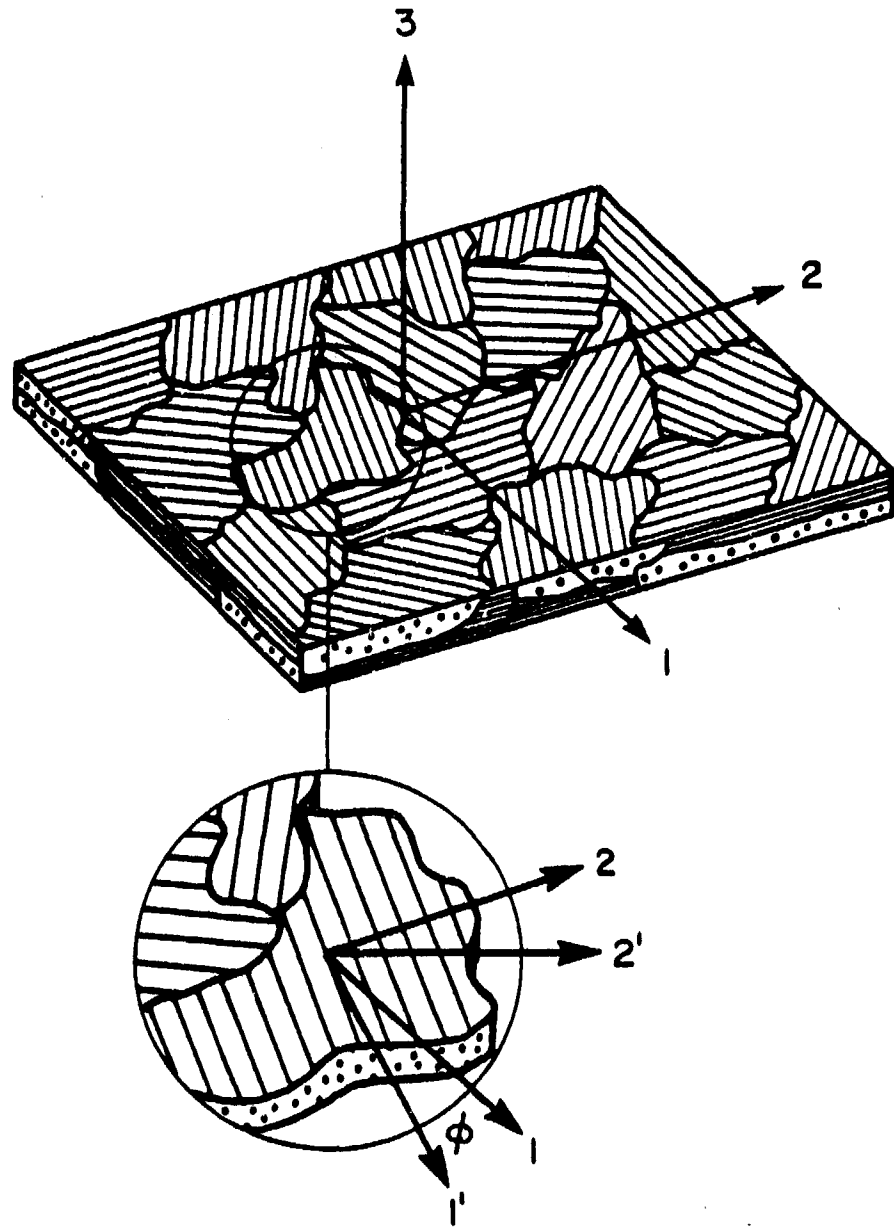


FIGURE C-2 Schematic definition of the aggregate model for sheet molding (McCullough et al., 1983).

The distinction between the two-dimensional and three-dimensional orientation distributions can be illustrated by (1) assuming an infinitely long aspect ratio, (2) approximating the longitudinal and transverse elastic constants by the respective Young's moduli, and (3) referring to the respective "random" states of orientation.

Lavengood and Goettler (1971) used these approximations to generate a rule-of-thumb expression for the modulus of a structure having three-dimensional random fiber orientation

$$\bar{E}_1 = \frac{1}{5} E_{11} + \frac{4}{5} E_{22}$$

where E_{11} and E_{22} are the longitudinal and transverse engineering stiffnesses for a unidirectionally oriented ply. At 30 volume percent loading, this equation predicts a value about 20 percent lower than the in-plane stiffness for random two-dimensional orientation. A rule-of-thumb expression for the latter is

$$E_1 = \frac{3}{8} E_{11} + \frac{5}{8} E_{22}$$

Halpin and coworkers (1971) treated the orthogonal 3-dimensional problem by modeling a plain, square woven fabric pierced by a straight yarn perpendicular to the fabric plane. Results showed that the moduli in the plane of the woven fabric in the 3-dimensional case were about 5 percent lower than the comparable moduli for the 2-dimensional material (plain-square weave) at 50 volume percent loading. Thus, the 3-dimensional weave overcomes the low shear strength between layers of a 2-dimensional fabric laminate with only a small sacrifice in laminate in-plane stiffness.

The role of fiber aspect ratio can be illustrated for a perfectly collimated array of aligned fibers with a uniform aspect ratio. Table C-2 and Figure C-3 summarize the situation for the two-dimensional plane-stress stiffness problem for the glass-epoxy system. Clearly the modulus depends on the fiber aspect ratio, the volume fraction of fibers, the fiber-to-matrix modulus ratio, and the fiber orientation distribution. Note particularly in Figure C-3 that, for a unidirectionally oriented ply, the critical aspect ratio has almost no dependence on fiber volume fraction but does significantly depend on the fiber-to-matrix modulus ratio (Kardos, 1985). A fictitious five-fold increase in E_f/E_m (keeping E_m constant) increases the critical aspect ratio (at which the continuous fiber modulus is approached) from about 100 to over 200 for a fiber volume fraction of 0.5. These same aspect ratio dependencies are reflected in any fiber orientation distribution, including that of random-in-plane.

The reality of a distribution of fiber aspect ratios that can result from breakage in extrusion and injection molding equipment can be estimated from special treatments (Halpin et al., 1971). However, no general treatment is available that specifically displays the appropriate role of the statistical parameters of a distribution of aspect ratios.

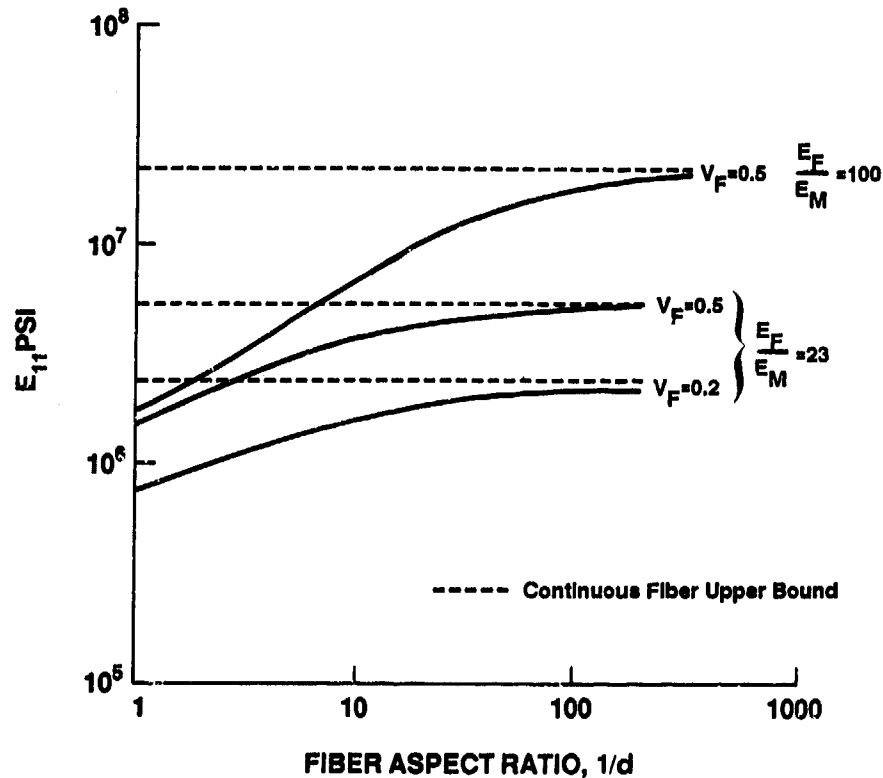


FIGURE C-3 Effects of fiber aspect ratio, fiber volume fraction, and fiber-to-matrix stiffness ratio on the longitudinal stiffness of unidirectionally oriented, short glass fiber-epoxy composites (Kardos, 1985).

Dimensional stability (i.e., expansion coefficients) during temperature excursions or exposure to swelling environments is a stiffness-dominated phenomenon that depends on the same parameters as stiffness as well as the dimensional stabilities of the fiber and matrix. Two-dimensional geometries have been treated (Kardos, 1973). However, the three-dimensional situation is more complicated, and reliable design formats are not yet available.

For both stiffness and dimensional stability, essentially continuous fiber property levels can be achieved if the fiber aspect ratio is high enough (see Figure C-3). In many short-fiber systems, however, the important ratio is not

the individual fiber aspect ratio but a fiber bundle aspect ratio (Kardos et al., 1983; McCullough et al., 1983; McGee, 1982; McCullough, 1983). For processes involving molding compounds, which are basically encapsulated fiber bundles, it is rare to find well-dispersed individual fibers in the final part. The degree of adhesion at the interface does not affect stiffness and dimensional stability (Kardos, 1984). All that is required is that there be good material contact (i.e., no voids at the interface).

The preceding approaches to predicting effective (average) properties assign equal weight to all material elements. This assertion is appropriate for thermoelastic and transport properties. However, these treatments cannot be rigorously extended to those properties for which the "weak link" elements dominate behavior (e.g., strength).

Although substantial progress has been made, it is clear that more work is required to provide a general rigorous format for predicting the stiffness, dimensional stability, and transport behavior of short-fiber composites.

STRENGTH

The short-fiber strength problem has been treated in terms of the laminate analogue model described earlier (Halpin and Kardos, 1978). Again the problem is separated into describing the behavior of a single unidirectionally oriented ply and then viewing the laminate as a combination of unidirectionally oriented plies. The longitudinal strength of a unidirectionally oriented short-fiber ply depends, in addition to those factors mentioned for stiffness, on the strength of the interface, the strength of the fiber, and, in ways different from the stiffness, on the fiber (or bundle) aspect ratio. Unlike for stiffness, continuous-fiber composite strengths cannot be attained in discontinuous-fiber systems, even at extremely high aspect ratios (Chen, 1971) (see Figure C-4). For unidirectionally aligned systems, the plateau strength values in the fiber direction for very high aspect ratios rarely exceeds 70 percent of the strength of continuous-fiber systems at the same fiber content. Furthermore, the critical aspect ratio, at which the maximum strength is achieved in short-fiber systems, is usually much higher than that needed to achieve the maximum (continuous-fiber) stiffness for the same fiber volume loading in the same system. One can appreciate this point by comparing Figures C-3 and C-5 at a fiber volume fraction of 0.5. In the case of strength, the plateau value is attained at an aspect ratio of about 500, whereas the critical aspect ratio for stiffness occurs at about 100. This difference in critical aspect ratios between strength and stiffness depends on the interface condition and the fiber-to-matrix stiffness ratio, as well as the fiber volume fraction.

The strength of a uniaxially aligned, short-fiber ply may be estimated by using a strength-reduction factor (SRF) approach developed by Kardos and co-workers (1980). The SRF is defined as the uniaxially aligned, short-fiber system strength divided by the strength of an aligned continuous fiber system having the same volume fraction of fibers. As the aspect ratio approaches unity, the SRF approaches that for a sphere-filled system. The SRF at large

GLASS FIBER/EPOXY COMPOSITES

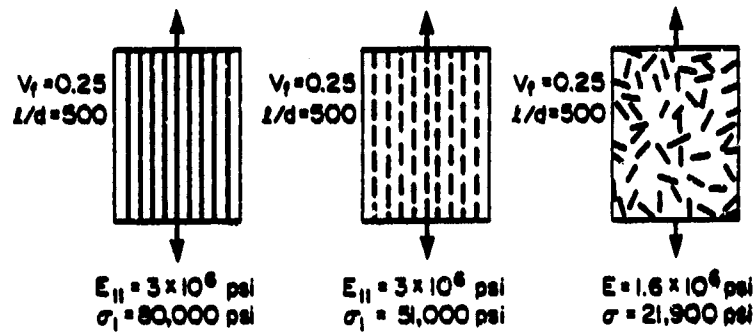
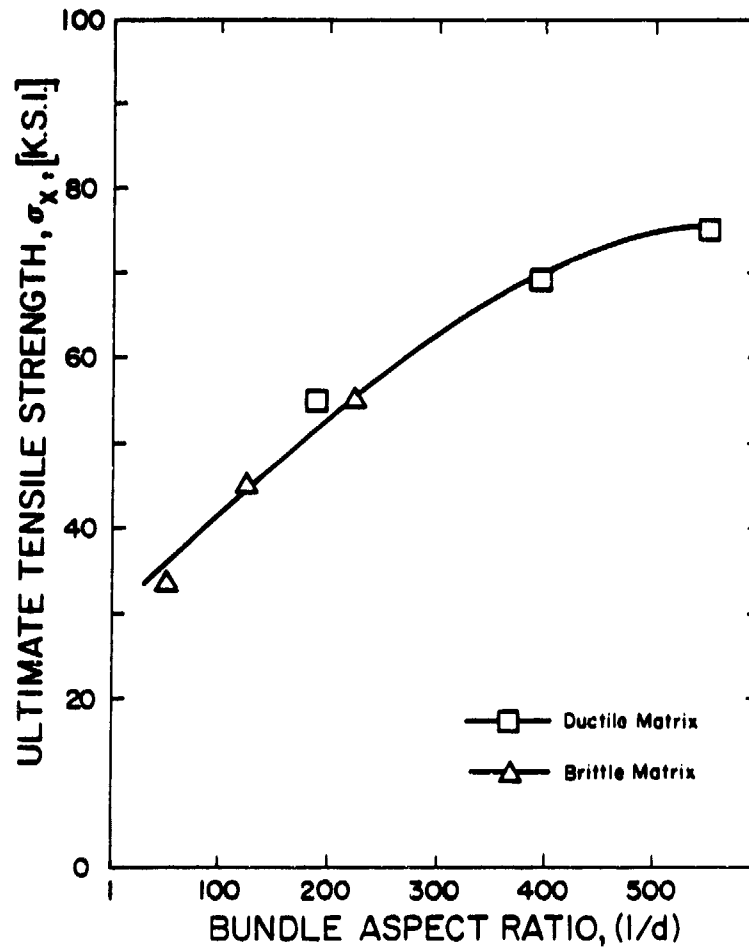


FIGURE C-4 Glass fiber-epoxy composites (Kardos, 1983).

FIGURE C-5 Dependence of longitudinal tensile strength on the bundle aspect ratio, l/d , for ductile and brittle epoxy matrix systems containing 50 volume percent aligned glass-fiber bundles (Kardos et al., 1983).

fiber-aspect ratios, where the plateau behavior is observed, is a weak function of fiber volume fraction (Kardos et al., 1980).

The second portion of the strength calculational format requires the choice of a failure criterion. One must decide what phenomenon governs the failure of the individual plies in the laminate as it is stressed and strained. From among a number of possible choices, the maximum strain criterion seems to adequately describe glass fiber-epoxy results (Halpin and Kardos, 1978).

To calculate the strength for a random-in-a-plane short-fiber composite, one utilizes the SRF along with the ply moduli to calculate failure strains for each ply in the laminate. As the laminate is strained, ply failure stress levels are noted and the laminate moduli are recalculated after each ply failure. The strength is the sum of the increments of stress the laminate went through until the last ply failed.

Figure C-6 shows the predicted strength for a random-in-a-plane fiber orientation, along with experimental data from both brittle and ductile matrix, glass-epoxy systems. The prediction is for the brittle matrix system; it provides a reasonably good (and conservative) engineering estimate of the strength. Reasonable predictions using this approach have also been achieved for nonrandom orientations (Kardos et al., 1983).

There are a number of important issues that emanate from this approach. The degree of adhesion is extremely important and is reflected in the interface strength term. This term is not predictable and is extremely difficult to measure experimentally (Piggott, 1982). The use of single-fiber pull-out tests may be misleading because these results do not account for the very important fiber-fiber interactions in the composite. The strength of flaw-sensitive fibers such as glass is dependent on fiber length, and the intrinsic strength of the actual short fiber must be used in any predictive format. The three-dimensional short-fiber strength problem has barely been touched and will certainly become a more important issue as these systems head toward uses as primary structural materials.

While initial efforts have focused on linear stress-strain behavior for the two-dimensional case, the nonlinear response deserves additional work. There is no three-dimensional analysis currently available for prediction of strength of short-fiber-reinforced systems.

FRACTURE TOUGHNESS

The fracture toughness of oriented polymeric composites is probably one of the least understood of all the mechanical responses. For most composites, including short-fiber systems, a sometimes espoused rule of thumb is that, as the strength increases, the toughness decreases. Thus it might be implied that, as the degree of adhesion increases, the toughness should decrease. While this is true generally for continuous-fiber-reinforced brittle matrixes, it is not always the case for particulate-filled systems (Bramuzzo et al., 1985) or for short-fiber-reinforced thermoplastics (Wambach et al., 1968).

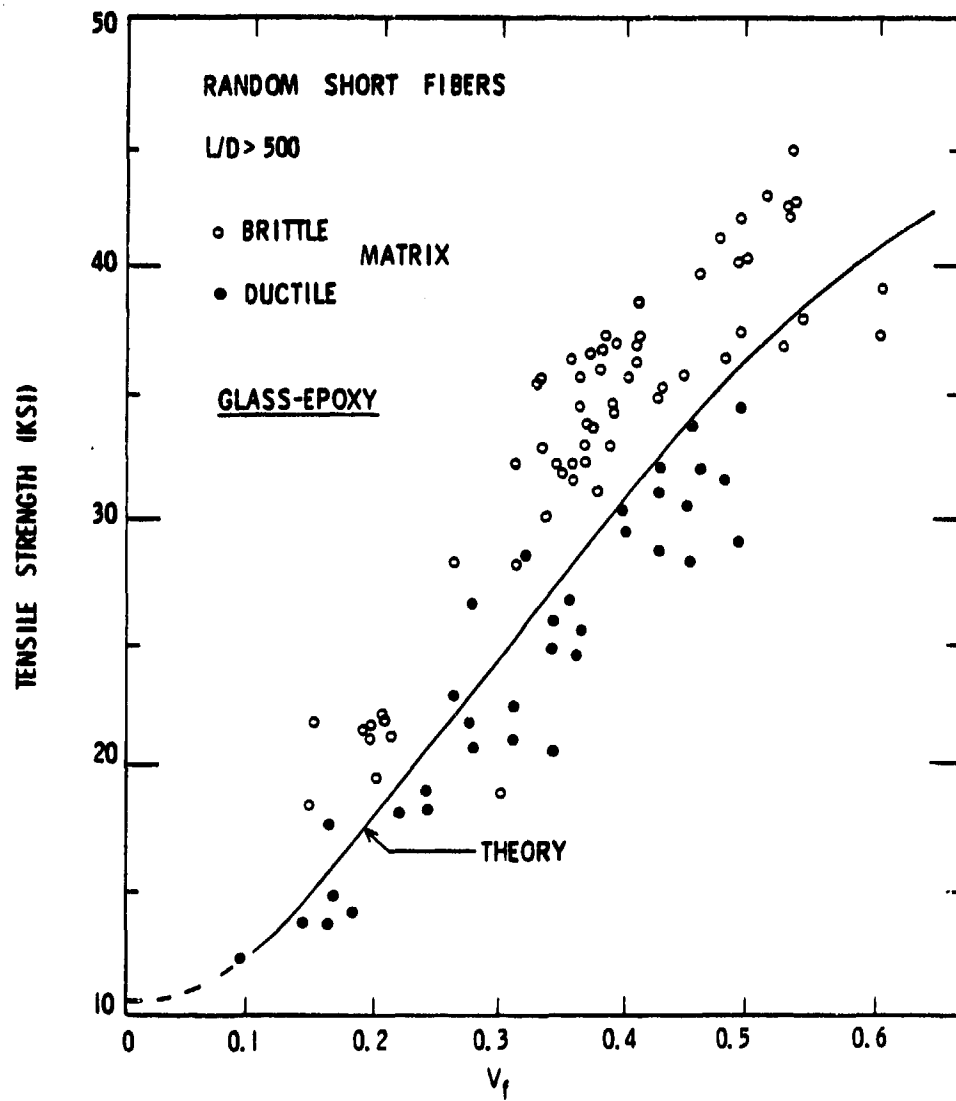


FIGURE C-6 Theory using the laminate analogy and maximum strain failure criterion (solid line) for two-dimensional random orientation. Note difference between brittle and ductile matrix data (Halpin and Kardos, 1978).

Figure C-7 summarizes qualitatively some of the results obtained by DiBenedetto and coworkers (Wambach et al., 1968; DiBenedetto and Wambach, 1972; Trachte and DiBenedetto, 1971). Improving the adhesion in a short-glass-fiber, polyphenylene oxide system actually increases the fracture toughness as measured in a double-edge-notched tensile test. Friedrich (1985) has presented similar findings for a variety of thermoplastic matrix systems. The same trend is clear in the glass-bead, PPO system. Thus the reinforcement geometry and the matrix ductility are important fracture toughness considerations.

Although various attempts have been made to increase toughness by adding a ductile third-phase material either dispersed in the matrix or selectively located at the interface, there is still no good format for predicting, *a priori*, the toughness of a composite system. A start toward this goal has

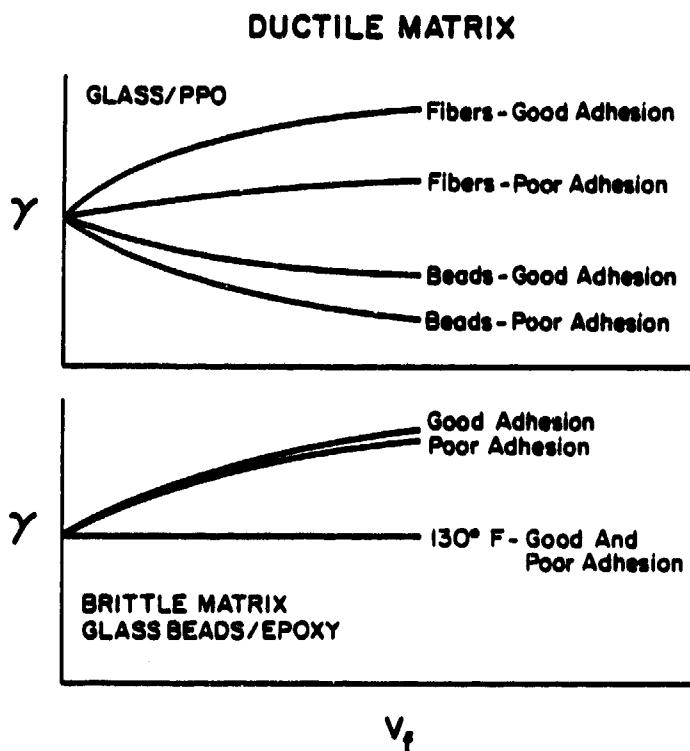


FIGURE C-7 Qualitative effects of reinforcement geometry, matrix ductility, degree of adhesion, and volume loading on the fracture toughness of glass-reinforced plastics (Wambach et al., 1968; DiBenedetto and Wambach, 1972; Trachte and DiBenedetto, 1971).

recently been made by Lauke and coworkers (1985) who have attempted to develop a theoretical micromechanical interpretation of fracture work in short-fiber-reinforced thermoplastics. Although their approach is a good start, it neglects fiber interaction. Tsarnas and Kardos (1985), utilizing the general micro-macromechanics, laminate analogy described earlier, expressed the fracture toughness, measured in a double-edged-notched tensile test, as a function of the elastic moduli, strength, and stress intensity factors of unidirectionally aligned, short-fiber plies.

Figure C-8 shows the predicted toughness values (solid lines) for two different fiber volume fractions for random-in-a-plane fiber orientation in a glass-epoxy system. Also shown are the experimental data, which contain considerable scatter. The predictions indicate a weak critical aspect ratio effect, although the experimental scatter makes it difficult to corroborate this prediction.

There is a paucity of data on the toughness of well-characterized short-fiber-reinforced thermoplastics. There is an urgent need for both theoretical and experimental work on the toughness of these systems, particularly as a function of fiber orientation distribution.

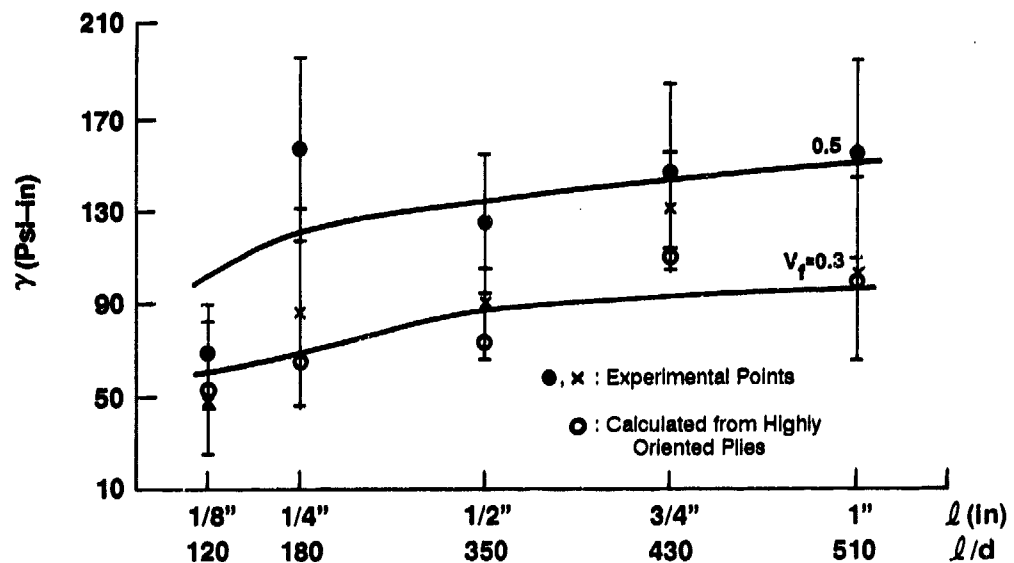


FIGURE C-8 Fracture toughness versus fiber bundle aspect ratio (length) for isotropic random-in-a-plane fiber orientation (Tsarnas and Kardos, 1985).

TIME-DEPENDENT BEHAVIOR

For cases of very lightly loaded structures, creep and fatigue are not normally a problem; however, it is extremely difficult to know at what precise stress levels time-dependency begins to become important. Historically, the temptation has been to unknowingly push short-fiber-reinforced thermoplastics into performance load ranges in which time-dependency produced dimensional instability as well as eventual failure. Exactly how time-independent fibers perturb the time-dependence of neat polymer is a crucial question.

Generally, it is observed that a moderately reinforced polymer (up to 40 weight percent randomly oriented short glass fibers) will retain the time- and temperature-dependent characteristics of the matrix polymer, except that (1) the modulus at a given strain level is proportionately higher and (2) the maximum extent of the plastic deformation that can be sustained before fracture will diminish (Matsuoka and Ryan, 1983). Scaling rules have been established for both glassy and crystalline polymers (Matsuoka et al., 1978; Matsuoka, 1985) that allow the prediction of creep and stress relaxation behavior from scaled stress-strain data. In the case of glassy matrix polymers whose stress-strain curves are congruent, creep and stress relaxation, as well as high-speed stress-strain behavior, can be predicted through a proper parametric extrapolation of laboratory stress-strain data obtained at constant strain rate. For crystalline polymers whose stress-strain curves are not congruent, behavior at higher strain rates or at decreased temperatures can be predicted by multiplying the stress and dividing the strain by the same scaling factor--namely the strain rate raised to a constant power (between zero and one).

Since the time-dependence of mechanical and aging behavior of a glassy polymer is predominantly affected by how far the temperature is below the respective T_g , the use of a glassy polymer with a high T_g for the matrix will result in less tendency for composite creep. The subject of physical aging for glassy polymers is an extensive study in itself, but in general a glassy polymer matrix with a higher T_g tends to age more slowly.

Crystalline polymers tend to creep more than glassy polymers in general, but tend to retain the partial rigidity and strength to quite high temperatures, and thus the effect of reinforcement is often very dramatic. Filled crystalline polymers will creep much less than the same unfilled polymer, particularly at high temperatures.

Solvents and solvent-like agents affect the time-dependent behavior of polymers and polymer composites. At very small concentrations, solvents can accelerate physical aging and can cause apparent loss of flexibility and plasticity, resulting in embrittlement. This phenomenon has been called, somewhat misleadingly, antiplasticization. At higher concentrations the creep tendency, as well as a tendency to stress-crack or to undergo time-delayed static failure, is enhanced.

Since time- or rate-dependent strength criteria can be interpreted in terms of the competing effects between the stress to craze-crack versus the stress to shear-yield, and since the latter stress becomes greater with

increased strain rates and/or at lower temperatures, a systematic study of the time-dependent mechanical behavior of both reinforced and neat polymers is essential to understand the complex nature of the fracture phenomena in composite structures.

Jerina and coworkers (1982) and Nicholais and coworkers (1981) have superimposed composite micromechanics on a time-dependent matrix to predict time-dependent composite behavior.

Of the myriad issues facing the advancement of short-fiber reinforced polymer technology, the characterization and prediction of time-dependent behavior may eventually be the most crucial.

WEARABILITY

Wear is the deterioration of a body at and near the surface caused by prolonged and often repeated applications of abrasion. In polymers the wear can be caused by direct mechanical abrasion or, in some cases, by thermal degradation due to the heat generated by the mechanical work of abrasion. In either case, the process of wear exhibits features similar to dynamic mechanical loading during which the stress is applied in cycles. Wear depends not only on material properties, the surface morphology, the molecular weight, the glass transition temperature, and the fillers and other additives, but also on the material against which the composite is abraded. One method of testing the wearability of a polymer is to install a sample on a rotating disc and to rub it against another surface of either the same or a different material under a load (Hertzberg and Manson, 1980). The wearability is sometimes shown to correlate with dynamic mechanical properties or with the fatigue properties (Brown, 1981). Wearability of fiber-reinforced plastics depends on exposure of fibers at the free surface. Exposed fibers or shallow embedded fiber can be broken and extracted on abrasion, leading to a highly irregular surface that has even greater susceptibility to wear. A resin-rich surface shows the best wear characteristics. Matrix selection, reinforcement selection, and processing conditions strongly influence the surface characteristics of fiber-reinforced plastics.

PROCESSING SHORT-FIBER COMPOSITES

During the past 20 to 25 years, a variety of high-performance thermoplastic materials has been developed and commercialized (Titow and Lanham, 1976; Folkes, 1982; Modern Plastics Encyclopedia, 1984; Griffiths et al., 1984; Kamal and Lafleur, 1982; Plastics Processing, 1982; Ziegmann and Menges, 1978; Turkovich and Erwin, 1983; Alfrey, 1976; Motoyoshi and Takada, 1982; Schweizer, 1982; Ferry, 1971; Fredrickson, 1964). These represent the majority of products now lumped together in a class of materials referred to as engineering plastics. Because of the thermoplastic nature of the resin matrix, these short-fiber-reinforced thermoplastic composites can be processed by a variety of techniques. Although each of these techniques is distinctly different from the others, they all involve a series of common sequential steps:

- Heating composite to form mobile liquid form (i.e., melt)
- Forming part from composite melt
- Cooling part to temperature below solidification point
- Removing formed part from mold

The most common molding techniques are summarized in the following sections.

It is now well understood (Ferry, 1971) that for a polymer to exhibit mechanical integrity in the solid form it must have a molecular weight that exceeds the critical entanglement value. Thus thermoplastic materials of commercial worth almost always exhibit a high viscosity. Some thermoplastic material such as polyphenylene sulfide and a certain class of polyimides cross-link during molding so that the initial viscosity may be very low, but they are exceptions. Thus the major processing problems for thermoplastics are predominantly related to the high melt viscosity that is manifested in various forms such as poorly knit weldlines, uncontrolled orientation, an insufficiently filled cavity, and large power consumption. Thermal degradation during processing can also be a result of the high viscosity, which could cause the polymer melt to stagnate locally. When fillers such as short fibers are added, these problems often can be greatly magnified.

Because the polymer relaxation process is not characterized by a single time but by many relaxation times, the steady-flow viscosity of the melt is the cumulative sum of many single rate processes. Empirical forms of expression such as the power law are frequently invoked to describe the behavior (Fredrickson, 1964). However, such a constitutive equation neglects the viscoelastic nature of a polymer melt and, when incorporated in mathematical formulations such as a finite element analysis, fails to predict the residual stresses.

A significant issue in processing short-fiber composites is that the rheology of fiber-filled melts is not understood, even for simple flow geometries.

INJECTION MOLDING

A pelletized molding compound ready for injection molding is supplied by mixing the reinforcing fiber with base resin in the melt phase, passing the homogeneous mixture through a suitable die (i.e., hole, slot, etc.), and then chopping or rough-grinding the solidified mixture.

During the injection molding process the short-fiber composite, most often in pellet form, is fed through a feed hopper into the heated barrel of an injection-molding machine. In the barrel the resin matrix portion of the pellet is heated to a temperature above the melting point (semicrystalline base resins) or softening point (amorphous resins) of the matrix resin. This process produces a "melt" composed of a mixture of liquefied polymer and reinforcing fiber. The melt is continuously mixed and transferred down the

barrel by a rotating screw located in the barrel. When the melt reaches the end of the barrel, it is injected under high pressure through a small opening (i.e., gate) into a closed metal mold. In the mold the melt is forced through an opening (i.e., sprue) into the vented mold cavity, which has been precisely machined to desired finished-part specifications. The mold is maintained at a temperature below the solidification point of the matrix resin. After the part has solidified, the mold opens, the finished part is ejected and the mold closes, ready for the next molding cycle.

In this simplified summary of the injection molding process, reference was made to the melt and the process whereby it was forced under pressure into a closed mold. The movement of the melt down the barrel and into the mold under pressure subjects the polymer molecules to shear forces. As shear is increased, thermoplastics exhibit non-Newtonian behavior. At the high shear rates often encountered in injection molding, these materials become increasingly pseudoplastic, and apparent viscosities decrease, often by several orders of magnitude. Addition of short fibers to a thermoplastic matrix causes an increase in melt viscosity. At low shear rates this difference can be appreciable. However, at high shear rates (e.g., 10^4 to 10^5 sec^{-1}) this difference can become much smaller, meaning that the reinforced composites might mold much like the base resins. This similarity in high shear viscosity for unreinforced and short-fiber-reinforced thermoplastics is an important factor in the successful use of these materials in injection molding applications. Typical shear rate response curves for reinforced and nonreinforced thermoplastics are given in Figure C-9.

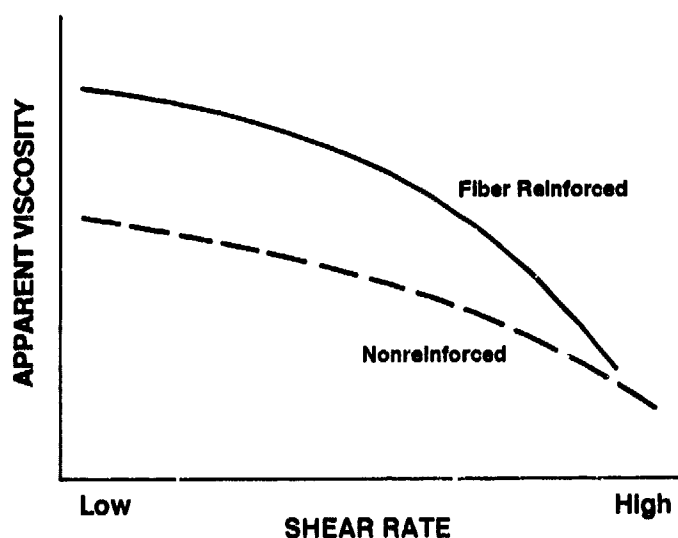


FIGURE C-9 Shear rate response curves.

Control of fiber orientation during processing is probably the most important factor underlying the efficient use of short fibers in composites (Johnson, 1983). The very nature of the injection molding process, which involves fast movement of a melt into a mold that is often very complicated in shape, leads to little control of fiber orientation. It is nearly impossible to predict *a priori* the fiber orientation distribution that will occur during injection molding of a short-fiber composite part. However, Goettler (1970 and 1984) has shown that gate and mold geometry, fill (flow) rate, viscosity, fiber loading, channel diameter-to-fiber length ratio, fiber aggregation state, pressure changes, and flow instabilities all are important in controlling the final fiber orientation distribution in injection molding as well as in extrusion and transfer molding. Goettler utilized this basic knowledge to design an expanding mandrel tube extrusion die that aligns short fibers in the circumferential direction of the extrudate (Goettler, 1983). Advani and Tucker (1985) described three-dimensional orientation distributions in terms of fourth-order tensors and attempted to relate these tensors to the rheological properties of fiber suspensions, thereby building a bridge between processing parameters and final performance properties.

In recent years more and more attention has been given to computer modeling of the injection-molding process. When perfected, this technique will result in a marriage of mold design and processing parameters that will allow the design engineer a greater freedom and higher level of confidence in designing structural components from short-fiber-reinforced composite materials.

The nature of the injection-molding process also limits the fiber length. The action of the screw in the barrel, which mixes and transports the resin-fiber melt, causes significant fiber breakage, as does the compounding step used to mix and pelletize the reinforced composite. In addition, narrow openings and passages in the mold can have a significant effect on fiber breakage. Under ordinary operating conditions, maximum fiber lengths in the final molded part will be in the 50 to 500 μ range regardless of the starting fiber length. Naturally, this phenomenon plays an important role in limiting the maximum properties that can be achieved in an injection-molding process (Filbert, 1969). Special compounding and pelletizing procedures can be used to produce pellets containing long (e.g., 0.12 to 1 in.) reinforcing fibers. Processing of these materials in special injection molding equipment utilizing molds with unrestricted passages can produce moldings with somewhat preserved fiber length. However, this is not yet a widely used technique, and further developments are needed. Innovation in manufacturing methods which result in greater fiber length can be expected to increase material strength and toughness.

Machine and mold wear are important considerations in processing fiber-reinforced thermoplastic composites. The combination of high temperature and abrasive fibers (e.g., steel, glass) can present a problem unless proper precautions are taken. Special barrels and screws (e.g., hardened steel, nitrided steel) are recommended for compounding and molding equipment as well as for molds. If these precautions are taken and proper attention is paid to processing conditions, wear problems can be minimized or eliminated.

The injection-molding technique produces parts quickly and is ideal for mass production of small parts. Since molds are usually quite expensive, it is desirable to use this technique in applications requiring high-quantity parts to take full advantage of the economy offered by the fast, low-labor-intensive procedure. Although production of large parts (i.e., greater than 30 to 40 pounds) by this technique is limited by machine size, recent advances and current programs promise to change this situation and allow routine production of large parts. Typical parameters for processing short-fiber-thermoplastic composites by injection molding are given in Table C-3.

TABLE C-3 Injection Molding of Short-Fiber-Thermoplastic Composites*

Processing Parameter	Value
Machine type, preferred	Reciprocating screw
Processing temperature, °F	600 to 800
Molding pressure, 10 ³ psi	5 to 40
Injection speed	medium
Screw speed	medium
Back pressure, psi	<50
Compression ratio	1 to 3
Shrinkage, %	0.05 to 0.5

*Value ranges given for a select class of high-temperature thermoplastic composites including PPS, PEEK, PEI, PAI, PES, PAS, polyacrylate, etc.

An important issue is that the prediction and control of fiber orientation distribution is one of the most difficult but most important problems now hindering the advancement of short-fiber composite technology.

COMPRESSION MOLDING

Although compression molding is a processing technique most commonly used with thermoset composites it can be, and is, used in the processing of thermoplastic composites. With short-fiber thermoplastic composites the raw material, generally in pellet or chopped rod form, is placed in a heated mold cavity, the mold being located in a hydraulic press. Pressure is applied and the composite material flows under the influence of heat and pressure to fill the mold cavity. Utilization of this process for thermoplastic composites is small in volume and generally quite specialized. The general process is diagrammed in Figure C-10.

In compression molding, mold costs are generally low because of the simplicity in part design. In addition, fiber length can be maintained because there is no mixing or mastication of the composite during molding.

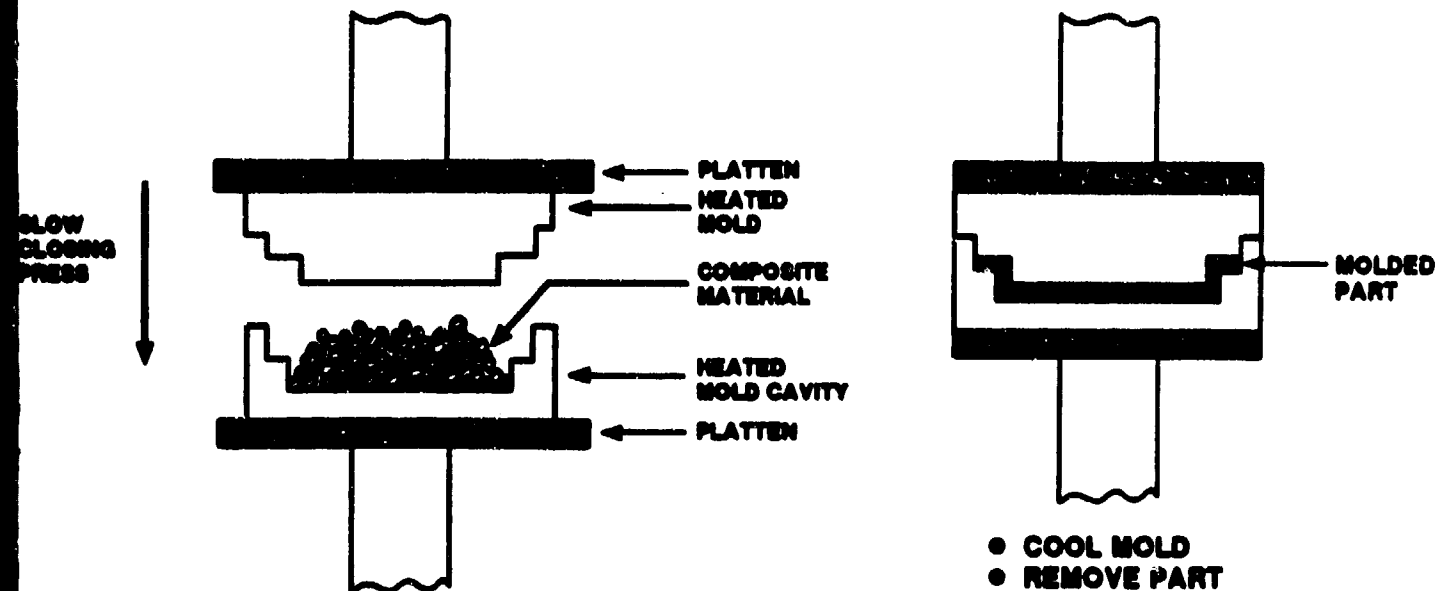


FIGURE C-10 Compression molding process.

Fiber orientation does not occur during the molding process, so generally a homogeneous part is produced. However, cycle times are long compared to injection molding, and complex shapes are not as easily molded. Since each mold cavity must be loaded individually, use of this technique for small parts is generally not recommended. General characteristics of compression molding are compared with injection molding in Table C-4.

STAMP MOLDING

Stamp molding is a rapid molding process used to form parts from glass or carbon fiber-mat-reinforced thermoplastic composites. The process in reality is a rapid compressing molding technique, but it is often referred to as "thermoplastic composite stamping" because of similarities to conventional metal stamping. During this overall process, precut sheets (blanks) of thermoplastic composite containing fiber-mat reinforcement are first heated in a suitable oven to a temperature of about 50 to 100°F above the melting or softening point of the matrix resin. The heated blanks are then stacked and rapidly transferred to a positive-pressure mold cavity located in a fast-closing hydraulic or mechanical press. The press closes and, under pressure, the fiber mat flows along with the matrix resin to fill the mold (Figure C-11). Since the mold is maintained at temperatures well below the solidification point of the matrix resin, the part rapidly solidifies and is

TABLE C-4 Short-Fiber Composite Molding Techniques

Technique	Fiber Form	Raw Composite Form	Nominal Cycle Time, sec	Molding Pressure, psi	Mold Cost	Process Cost
Injection molding	Very short	Pellets	20 to 240	10,000 to 20,000	High	Low
Compression molding	Short to long	Pellets, sheet, chopped rod	Hours	1,000 to 5,000	Med.	High
Stamp molding	Continuous chopped mat	Sheet	30 to 300	2,000 to 6,000	Med. to High	Med.

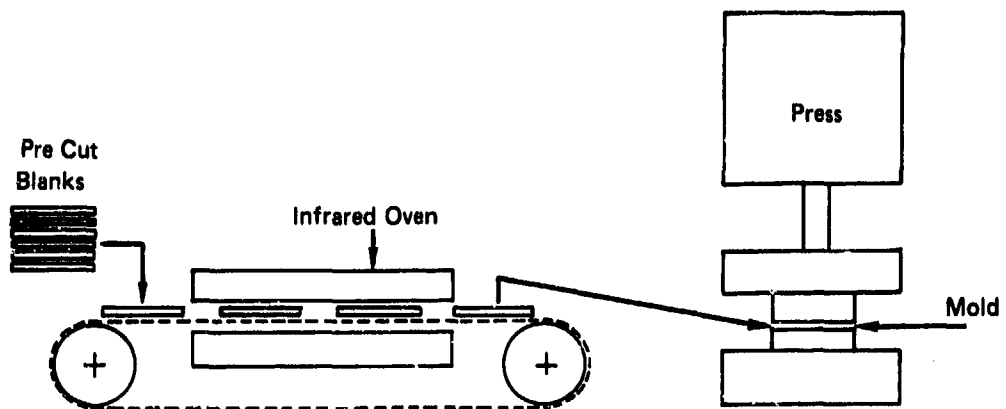


FIGURE C-11 Stamp molding process.

removed from the opened mold when sufficient part rigidity is obtained. Pressure is maintained during the cooling and solidification process. Because fiber length is maintained, this molding technique produces high-strength, high-impact parts, and cycle times are often competitive with injection molding. General characteristics of this process technique are compared to injection and compression molding in Table C-4.

EXTRUSION

Extrusion is a well-developed and commercially successful technique for processing thermoplastic resins. Plastic bags, pipe, coated wire, certain gasket materials, film, and plastic window frames are all products of the extrusion process. In spite of this, extrusion of short-fiber thermoplastic composites has not been widely exploited, although there are some notable exceptions (McGraw-Hill, 1984), and this appears to be an area where significant progress can be made.

Basically, the process involves an extruder to form the composite melt and to transport the melt down the barrel of the extruder. At the end of the extruder the melt is forced continuously, under pressure, through a forming die to shape and cool the composite material. The composite exits from the die in final form. One can envision this process being used to fabricate a variety of reinforced composite structures ready for use in industrial and aerospace applications. A typical extrusion process is outlined in Figure C-12.

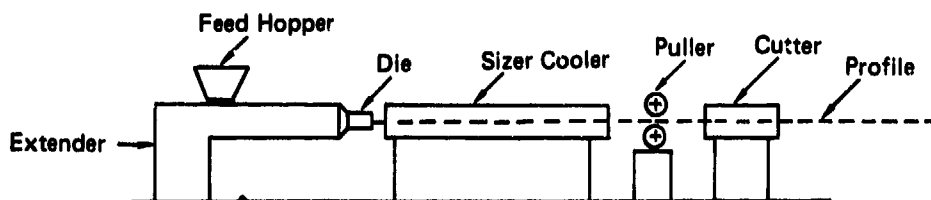


FIGURE C-12 Extrusion process.

COMPUTER-AIDED MANUFACTURING

Computer-aided manufacturing of composites and particularly short-fiber composites is still in its infancy. Although processing equipment, such as injection-molding machines, has been greatly automated, there is still no on-line, closed-loop control logic employed in which product quality is sensed and fed back to the processing unit. Research in this area is just beginning; its success will depend on the development of adequate sensors and sensing techniques in conjunction with advances in the areas of robotics and nonlinear control methodology.

QUALITY ASSURANCE

The major quality and performance issue facing the short-fiber composites industry is part and mold design. Too often ultimate composite properties

are not translated into the final part because of improper mold design and/or molding procedures. All part and mold design and molding operations must take into account fiber breakage, fiber orientation, flow patterns, weld lines, etc. Improper mold design can result in failure at stress levels as low as 25 percent of ultimate.

With proper attention at all phases of handling, from raw materials production to final part production, high-quality parts can be produced. If short-fiber composites are to be considered for high-performance parts, these issues are critical to success.

APPLICATION OF SHORT-FIBER COMPOSITES

Short-fiber-reinforced thermoplastics have seen increasing applications in the transportation industry. Here the emphasis has been on weight savings, which can be translated into better fuel economy. Many of these applications have been with glass fibers as the reinforcement phase. The new thermoplastic matrices of interest possess a higher temperature capability than the more mundane systems and could see service in hotter regions of transit vehicles.

A wide variety of industrial applications is open to these materials, such as power tools, appliance parts, water engineering and plumbing parts, mixing valves, chemical plant components, and a host of other types of components. The short-fiber systems of interest here would lend themselves to the more demanding applications in these general categories.

New applications of these materials have centered around the use of conductive reinforcements such as graphite fibers. These components have found widespread acceptance as electrical parts where some level of conductivity is desired. In this case the reinforcement provides not only mechanical property enhancement but also better electrical and thermal properties. There have been limited aerospace applications for components like electrical connectors and enclosures. These will tend to increase as new reinforcement schemes provide increased electrical properties. A greater confidence level will materialize with greater experience.

More extensive and demanding applications of these materials can be expected if a sound scientific basis can be established relating processing and materials properties. If this is not the case, these materials will not be used in primary structure applications. The issue, of course, is that relationships between processing parameters and final part performance properties are empirical at best and usually nonexistent. This results in expensive development programs on full-scale equipment and often prevents optimum processing conditions from ever being found.

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APPENDIX D

MORPHOLOGY-FIBER INTERACTION

The mechanical properties of fiber-reinforced plastics depend on the matrix to transfer stress to the high-strength fibers. This depends in turn on the nature of the fiber surface and the fiber-to-matrix interfacial bond. Improvements in the mechanical properties of the composite may result from changes in morphology and crystallinity of the polymer matrix in the interfacial region. In polyamides, reinforcing fibers produce a directional crystallization, with a difference in the crystallization around type I and type II carbon fibers and E glass fibers. The directional crystallization consists of an inner zone (the initial nucleation region adjacent to the fiber) and an outer zone (the columnar growth region, which extends to the spherulitic structure of the matrix). The width of the inner zone is greater for type I fibers. The extent and morphology of the columnar growth region around type I and type II fibers are similar, irrespective of fiber manufacturer. Similar columnar structures exist in polypropylene and polyetheretherketone nucleated at carbon fibers (Hobbs, 1971; Kardos, 1973; Hartness, 1984). The morphology and molecular orientation of the polymer lamella within the columnar zone are similar to that along the radius of a spherulite or a "row" nucleated structure (Keller, 1955). However, the nucleation of polymers on substrates is complex and may be influenced by factors such as supercooling, thermal conductivity, surface tension, surface energy, and polymer flow rates. In many cases the nucleation of polymers is considered in terms of the epitaxial matching of the crystal lattices of the polymer and substrate, where, in the initial nucleation, the molecular chain axis of the polymer is oriented parallel to the substrate surface (Hara and Schonhorn, 1972; Takahashi et al., 1970). Experiments using graphite surfaces have shown that the polyethylene unit cell is oriented with its (110) plane parallel to the substrate and has a lattice mismatch of less than 4 percent (Baer et al., 1971; Tuinstra and Baer, 1970).

Chemisorption has also been proposed as a nucleating mechanism that may aid epitaxial crystallization. The nucleation of polypropylene (Hobbs, 1971), nylon 6 (Baer et al., 1971), and nylon 66 (Frayer and Lando, 1972) onto graphite surfaces indicates that there are strong interactions between the polar groups of the macromolecule and the graphite crystallites. The chemisorption of atomic hydrogen, carbon, nitrogen, and oxygen are of particular importance; the stable configuration for carbon and nitrogen is

where the atoms are situated directly over the bond connecting nearest carbon atoms in the graphite substrate (Bennett et al., 1971).

In composite systems, consideration is given to the type of carbon fiber used since it is shown by Hobbs (1971) that polypropylene films containing type II carbon fibers do not generate a columnar growth, whereas type I fibers have nucleating ability. This is attributed to the difference in graphite crystallite size in the type I and type II carbon fibers; for nucleation a minimum graphite crystal size of 50 Å is required (Kardos, 1973). In the investigation of the morphology of polyetheretherketone on carbon fibers by Hartness (1984), similar growth was demonstrated by using HMS graphite fiber (type I) and AS-4 (type II).

Detailed studies have been carried out by Bessell and Shortall (1972) using cast thin films of nylon containing single graphite fibers. Results from these studies indicate that the columnar structure around filaments can be examined using polarizing optical microscopy and transmission electron microscopy.

Optical polarizing microscopy reveals a difference between the columnar structures surrounding the type I and type II carbon fibers and the glass fibers. The columnar region consists of an inner zone, adjacent to the fiber, with a fine speckled structure and an outer zone with a fibrillar structure extending to the spherulitic matrix. For type I carbon fibers the width of the inner zone is greater than around the type II fibers. The extent and morphology of the columnar regions around type I and II carbon fibers are similar irrespective of fiber manufacturer. "Modmor I," "Rigilor AG" (type I), and "Grafil BM-S" (I) have similar structures, and "Modmor II," "Rigilor AC" (type II), and "Grafil A" also produce similar structures.

No differences in the columnar growth exist with fiber surface treatments, and similar columnar morphologies surround treated and untreated "Hitron RMG-50" carbon fibers. This similarity is observed in films containing treated and untreated "Modmor I" and "Modmor II" carbon fibers.

Reduction in the matrix spherulite size effects the outer fibrillar zone of the columnar growth region around type I and type II carbon fibers. Decreasing the mean spherulite diameter from 25 µm to about 3 µm eliminates the outer zone in both cases. The inner white zone is unaffected and is independent of the nucleation and crystallization rates within the spherulitic matrix.

The ability of the glass fibers to nucleate columnar growth is less than carbon fibers, and the columnar structure around glass fibers is not apparent in some places along the glass filament.

The different nucleating ability of carbon and glass fibers is also apparent in bulk composite sections. Carbon fibers are always at the central nucleation position of each columnar unit. Glass fibers, however, are randomly positioned with respect to the spherulite or columnar structures.

Electron micrographs of the columnar crystallization at "Modmor I" and "Modmor II" carbon fiber surfaces show the columnar region extending out to the matrix spherulite structure. There are few nuclei on the glass fiber surface. This lack of nuclei produces a radiating fan-like structure initiated at points along the surface, in contrast to parallel fibrillar morphology around type I carbon fibers. The columnar zone around type II fibers exhibits these fan-like features, indicating fewer nuclei. The melt-crystallized films do not reveal morphological features corresponding to the inner nucleation zone in films examined using polarizing microscopy.

A difference in pull-out of fibers is pronounced in composites containing treated and untreated type I carbon fibers. For treated fiber, almost no pull-out and debonding occurs, whereas extensive debonding and pull-out takes place in the untreated fiber composite. This effect is not observed in composites containing type II carbon fibers.

From scanning electron micrographs the pull-out lengths can be measured. The analysis outlined by Phillips (1972) can be used to obtain values for the nylon-fiber interfacial bond strength and fracture energies (Table D-1). Note the high bond strength of treated type I fibers and a correspondingly low fracture energy value, indicating little energy dissipated in the pull-out of fractured fibers. The untreated type I fibers have a low bond strength and a high pull-out fracture energy. Surface treatment of the fibers does not have a pronounced effect on bond strength and fracture of composites containing type II carbon fibers, and the values calculated for type II carbon and glass fibers are similar.

Discussion

Various columnar structures exist at the fiber surface. Type II carbon fibers have a great nucleating ability for the polyamide. Crystallization around these fibers is more pronounced than that produced by the majority of other surfaces that promote directional crystallization.

Although columnar growth may exist around all the fibers examined, the columnar growth around carbon fibers is more pronounced than that surrounding glass fibers, and secondly, the structure around type I carbon fibers is finer than around type II fibers. This is due to variations in the nucleating power of the different fiber surfaces. Since all samples were prepared under identical isothermal conditions, thermal conductivity would not account for the differences observed.

The difference in the nucleating power of type I and type II carbon fibers is considered by examining the inner zone of the columnar growth observed in the polarizing microscope. Although the structure of this zone is similar around both fiber types, the width of the inner zone around type II fibers is smaller than that around type I carbon fibers. The inner zone is due to rapid nucleation of the nylon on the fiber surfaces. There are two reasons for this: the structure of the zone resembles that of nylon 6 spherulite nuclei when observed between crossed polars, and a decrease in the matrix spherulite diameter produces a reduction in the outer columnar zone and not the inner zone, indicating that the zone is formed prior to

TABLE D-1 Values of Interfacial Bond Strength and Fracture Energies Calculated From Fiber Pull-Out Lengths

Fiber	Mean Pull-Out Length (pm)	Bond Strength (MN m ⁻²)	Fracture Energies (kJ m ⁻²)		
			Pull-Out	Initiation	Total
Modmor I (treated)	3.6	479	0.65	0.03	0.68
Modmor I (untreated)	84.0	20	12.8	0.18	13.0
Modmor II (treated)	60.5	46	12.9	0.47	13.4
Modmor II (untreated)	47.0	60	8.5	0.3	8.8
Grafil MN-S (I treated)	11.7	181	2.8	0.06	2.9
Glass "E"	49.7	54	7.7	5.7	13.4

any substantial crystallization in the matrix. Because of the smaller width of the inner zone around type II fibers, these fibers have less nucleating power than type I fibers.

This reduction in nucleating ability is responsible for the coarse-fibrillar morphology and the formation of fan-like structures around type II carbon fibers and glass fibers. Since fewer independent nuclei would result in a reduction in the number of centers from which the nylon can crystallize, this results in a coarsening of the structure that fans out from individual nuclei.

As the number of nuclei increases, the growing crystallites quickly impinge on their neighbors and produce a more parallel fibrillar morphology, reducing the tendency to crystallize in fan-type structures. Apart from these differences in texture, the structure of the outer zone is similar to the radial structure of the spherulite. Similar growth rates apply, since the width of the outer zone is approximately equal to the spherulite radius, and a reduction in the spherulite diameter decreases the width of the zone.

There are several possible explanations for the differences in nucleating ability of type I and type II carbon fibers. Among these are the graphite crystallite size, crystallite orientation, surface smoothness, and perfection of the individual graphite crystallites. Both

Hobbs (1971) and Baer and co-workers (1971) conclude that crystallite size is the most important factor governing the nucleation of thermoplastics onto graphite fibers. Hobbs believes that, to effect the epitaxial nucleation of polypropylene, a minimum graphite crystal size of 50 Å is required. The crystallites in type II material are less well oriented (Mimeault, 1971; Johnson, 1971) and smaller (Tuinstra and Koenig, 1970) than those in type I fibers. However, crystallite size alone as an explanation for columnar growth is somewhat doubtful. According to Tuinstra and Koenig (1970), who determined the graphite crystal spacings using laser Raman spectroscopy, the apparent crystallite size of "Hitron BMG-50" and Morganite II fibers are similar, 80 and 50 Å respectively, although these fibers exhibit different columnar morphologies, the "Hitron" fiber behaving as a typical type I fiber and the Morganite fiber as a type II. The Morganite "Modmor I" fiber, which has a graphite crystallite spacing of 200 Å, has a type I columnar structure similar to that around the "Hitron" fibers.

Although many fibers do show a correlation between columnar structure and crystallite size, it seems likely that the extent of epitaxial nucleation is also dependent on the orientation and defect concentration of the graphite lattice. It is known that the high pyrolyzation temperatures used in the production of type I carbon fibers promote orientation and lattice perfection within the graphite crystallites (Johnson, 1971; Watt, 1970; Donnet and Dauksh, 1972), and without exception all type I fibers exhibit similar columnar structures. It is interesting to note that, if crystallite size alone were responsible for the nucleation of nylon, one would expect a greater number of nuclei on the type II fibers. This is not found, and some minimum crystallite size must be present for the formation of a stable nucleus; the perfection and orientation of the substrate lattice also contributes to the nucleation.

The surface treatments of carbon fibers, applied by the manufacturers to improve the interlamellar shear strengths, do not have any effect on morphology and extent of the columnar growth. Detailed examinations of treated carbon fibers indicate that the effective surface area (Mimeault and McKee, 1969) and the graphite crystallite size (Tuinstra and Koenig, 1970) are altered. These findings demonstrate that these parameters alone are not wholly responsible for the columnar nucleation. Examination of the carbon fibers using scanning electron microscopy does not reveal obvious differences in the topography of the surfaces; however, as a result of oxidizing treatments, smoothing (Harris et al., 1969) and roughening (Mimeault, 1971) of the fiber surfaces have been recorded. The relative smoothness of the fiber and its cross-sectional shape have no effect on the columnar growth, since fiber surface topography on a large scale does not affect nucleation at a molecular level.

Although surface treatments applied to the carbon fibers do not have any apparent effect on the nucleation of columnar growth, they did, in the case of type I fibers, produce a significant increase in the nylon-graphite bond strength, as measured from pull-out lengths. However, the nucleation of a columnar crystallization cannot account fully for the changes in fiber-matrix interfacial strength. It seems likely, therefore,

that in the nylon-graphite interface there are two separate processes, one responsible for the bond strength. The nucleation of columnar growth appears to be a physical process involving the matching of crystalline lattices that depend on the orientation, perfection, and size of the graphite crystallites. In contrast, the bond strength is considered to be a chemical process involving keying of side groups and chemical bonding.

The detailed chemistry of the interface is difficult to define because the lack of information on the precise commercial treatments applied to the fibers. The following points are, however, considered significant.

Most commercial treatments are oxidizing in nature and are either nitric or perchloric acid-based or involve oxidation at elevated (1273°K) temperatures. Examination of the fibers indicates that little or no change in surface topography occurs. However, various workers (Mimeault, 1971; Mimeault and McKee, 1969; Harris et al., 1969) have shown either pitting or smoothing of the surface as a result of treatment. The chemistry of graphite in the presence of strong oxidizing agents such as nitric acid and perchlorates shows that several important reactions may occur (Cotton and Wilkinson, 1966; Goan and Prosen, 1969):

- Separation of the graphite crystal layers from 3.35 Å up to 7 to 8 Å. This product readily absorbs chemicals such as water, acetone, and alcohols, which further increase the layer separation up to 18 Å
- Graphite oxide may be formed, the structure of which is of the type -C-O-C-, and may convert to C=O or -C-OH. These latter groups are acidic and will bond with polyamides.
- There is also evidence that the graphite hexagonal layers become buckled. The separation and buckling of the graphite may explain the results of Mimeault and McKee (1969), who suggested that the effective surface area of the fiber is tripled by treatment.

From these oxidizing reactions on the graphite surface several possible mechanisms for the nylon-carbon fiber bond may be proposed:

- Absorption of part or all of an amide molecule may occur into the enlarged graphite layers;
- Chemical bonding may also take place between the reactive acidic groups on the oxidized graphite surface and the carbonyl and imino groups of the nylon; and
- The buckling of the graphite layers may also promote a physical keying between the fiber and matrix.

Because of these reactions interfacial bond strength of type I fibers is increased by surface oxidizing treatment. Such treatments do, however, affect the extent of columnar morphology. The effect of surface treatment on the bond strength of type II fibers does not appear to be as pronounced as the type I materials. This is probably because of the fact that the graphite

content of type II fibers does increase the wettability of the fibers, giving improved composite fabrication properties.

Therefore, although modification of the matrix structure around the fibers could affect the mechanical properties of some fiber-reinforced polymer systems, surface treatment appears to have a more significant effect in the case of nylon 6 reinforced with type I carbon fibers.

The nucleating ability of glass fibers is considerably less pronounced than carbon fibers. Apart from the overall reduction in columnar growth, crystallization varies in a random manner. Because of the amorphous structure of glass, the lattice matching criteria for nucleation are invalid, and it can be considered that nucleation is due in some part to the organic sizing on the fiber surface. The dispersion of size is nonuniform. This may account for the irregularities in the columnar structure. The nucleation may be due to the size being locally dissolved in the polymerizing nylon (in which the temperature may reach 200°C), the dissolved size causing nucleation of the nylon. The influence of the surface coating in promoting columnar growth is indicated by a reduction in the amount of columnar crystallization if the surface coating is removed. Some nucleation is still apparent, however, due perhaps to surface features on the glass itself.

In the crystallization of anionically polymerized nylon 6 onto reinforcing fibers, fibers nucleate a columnar structure. The morphology of this structure is different around the carbon and glass fibers and around type I and type II carbon fibers. The extent of columnar growth decreases with decreasing matrix spherulite size and is unaffected by surface treatment. The nucleation of structure is due primarily to the physical matching of the graphite crystallites.

In the case of type I carbon fibers, the surface treatments have a very significant effect on the fiber-matrix bond strength that cannot be satisfactorily explained in terms of the columnar structure. In the case of treated fibers, little debonding and fiber pull-out take place, and low fracture energies are found. In the untreated fiber composite, extensive debonding and pull-out occur, and this reflects high fracture energies. It is therefore evident that, in addition to the physical process responsible for the columnar growth, chemical bonding also occurs between the nylon and the oxidized graphite surface.

The crystallization of nylon onto glass fiber surfaces is nonuniform and is influenced to some extent by the presence of the size coating on the fiber surface.

It is clear that the nucleation of polymers on substrates is complex and may be influenced by factors such as supercooling, thermal conductivity, surface tension, surface energy, and polymer flow rates. Microscopy reveals a difference between the polymer columnar structures surrounding the type I and type II carbon fibers and the glass fibers. These differences may significantly affect the mechanical properties of composites made from such fibers.

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APPENDIX E

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

R. BYRON PIPES earned B.S. and M.S. degrees at Louisiana Polytechnic Institute, an M.S.E. at Princeton, and his Ph.D. at the University of Texas. He is presently Dean, College of Engineering, University of Delaware, where he previously held the position of director of the Center for Composite Materials. His research interests are in experimental mechanics for composite materials.

DON G. BRADY received his B.S. degree at Southern Illinois University and his Ph.D. in organic chemistry at Purdue University. Since 1966, he has been with Phillips Petroleum Co., where he is now a division manager in the Research and Development Department. His research has focused on organosulfur, organohalogen, and organometallic chemistry, flame-retardant additives for polymers, engineering thermoplastics, and advanced composites.

HUGH H. GIBBS received his B.Sc. and M.Sc. degrees at Queen's College (Canada) and his Ph.D. in chemistry at the University of Illinois. He has been with DuPont since 1956 and is now a research associate in the Plastic Products and Resins Department there. His research has been in synthetic organic chemistry, mechanisms of organic reactions, synthesis and reactions of fluorocarbon compounds, polymer chemistry, high-performance composites, and polyimides.

J. TIMOTHY HARTNESS received his B.E. degree at the University of Dayton. He is now with BASF Structural Materials, Inc. in Charlotte, North Carolina. Prior to his employment with BASF Structural Materials, Inc. he was a research chemist at the University of Dayton Research Institute, on-site at the Air Force Materials Laboratory. His research interests are in thermoplastic composite development, characterization, and unique processing techniques.

JOHN L. KARDOS earned his B.S. degree at Pennsylvania State University, his M.S. at the University of Illinois, and his Ph.D. in polymer physics at Case Institute of Technology. He has been associated with Washington University in St. Louis since 1965 and is currently director of the Materials Research Laboratory there. His research interests include the chemistry, physics, and fabrication of composite materials; structure-property relations in reinforced plastics; polymer crystallization and morphology; and materials characterization techniques.

MORTON H. LITT was educated at City College of New York, where he received his B.S. degree, and at Polytechnic Institute of Brooklyn, where he received his M.S. and Ph.D. degrees. He worked at Manchester University, the State University of New York College of Forestry at Syracuse, and Allied Chemical Corporation before joining Case Western Reserve University, where he is professor of polymer science. His research has centered on ionic and free radical polymerization mechanisms, organofluorine chemistry, and mechanical and electrical properties of polymers.

SHIRO MATSUOKA earned his M.E. degree at Stevens Institute of Technology and his M.S.E. and Ph.D. degrees at Princeton. He has been at AT&T Bell Laboratories since 1959, and he now heads the Plastics Research and Development Department there. His research interests include the mechanical, electrical, and morphological properties of high polymers and molecular relaxation phenomena.

JOHN T. QUINLIVAN received his B.S. degree from Gonzaga University and his M.A. and Ph.D. degrees at Princeton. He joined the Boeing Company in 1968 and is currently Chief of Engineering Technology for the Advanced Composite Development Program. His research interests include the physical properties of macromolecules, toughening mechanisms of polymers, and damage tolerance considerations of advanced composite materials.

RICHARD WILKINS was educated at the University of Oklahoma, where he earned his B.S., M.S., and Ph.D. degrees. He is presently Director, Center for Composite Materials at the University of Delaware, and a Professor of Mechanical Engineering. Prior to his present position he was an engineering staff specialist at General Dynamics. His interests include research on the design and manufacturing of composites.